Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2018

Supporting Information for

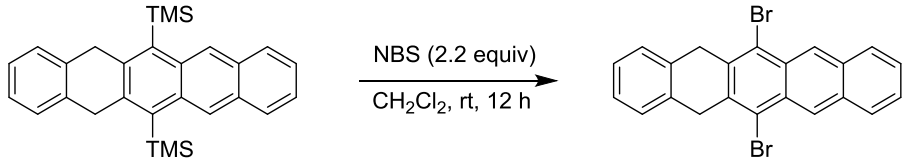
Lithiation of Palladated Dihydropentacene: New Route for Introduction of Substituents from Both of Electrophiles and Nucleophiles to Pentacene

Yanqing Wang, Kiyohiko Nakajima, Zhiyi Song and Tamotsu Takahashi*

Content

General Experimental Method: All reactions including air- and moisture-sensitive materials were carried out under atmosphere of nitrogen using standard Schlenk techniques. Tetrahydrofuran (THF), diethyl ether, toluene and benzene were distilled from sodium benzophenone ketyl under nitrogen. Starting material 6,13-bis-trimethylsilanyl-5,14-dihydro-pentacene was prepared according to the literature.[1] $Pd(PPh_3)_4$ was prepared according to the literature.[2] All the other reagents were commercially available and used as received. ^1H, ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$ or C_6D_6 solutions on a JEOL JNM-ECX400 or a JEOL JNM-ECA600 spectrometer.

Preparation of 6,13-dibromo-5,14-dihydropentacene 1.

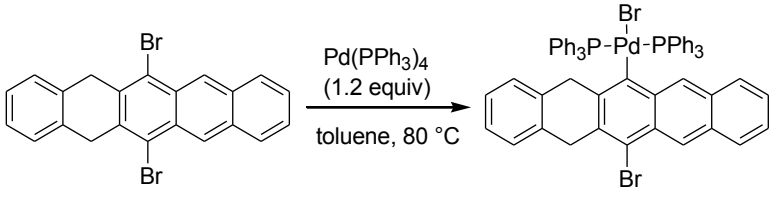


1

In a 50 mL Schlenk tube, under nitrogen atmosphere, 6,13-bis-trimethylsilanyl-5,14-dihydro-pentacene (783 mg, 1.84 mmol) and NBS (722 mg, 4.06 mmol) were dissolved in CH_2Cl_2 (10 mL) at room temperature. The mixture was stirred for 12 h at room temperature. The mixture was quenched with H_2O at 0 °C and extracted with $CHCl_3$. The organic phase was separated and washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated. The resulting solids were purified by a flash chromatography (silica gel, $CHCl_3$ as eluent) to afford the title compound **1** (363 mg, 45% isolated yield) as a solid.

1: ^1H NMR ($CDCl_3$, Me_4Si) δ 4.44 (s, 4 H), 7.27-7.29 (m, 2 H), 7.41-7.43 (m, 2 H), 7.52-7.55 (m, 2 H), 8.07-8.10 (m, 2 H), 8.92 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 38.2, 122.7, 126.5, 126.8, 127.1, 127.5, 128.3, 129.9, 132.3, 135.3, 135.4. HRMS (EI) calcd for $C_{22}H_{14}Br_2$: 435.9462. Found: 435.9460.

Preparation of palladated dihydropentacene 2.

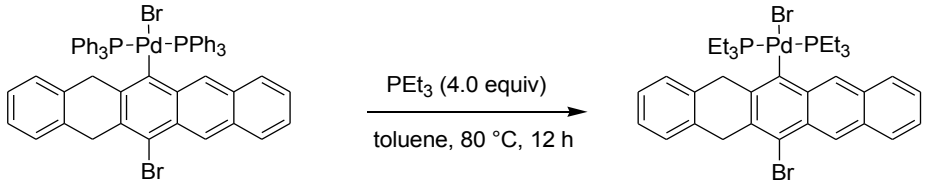


1 **2** 77%

In a 20 mL Schlenk tube, 6,13-dibromo-5,14-dihydropentacene **1** (16 mg, 0.0365 mmol) and $Pd(PPh_3)_4$ (51 mg, 0.0438 mmol) were dissolved in toluene (2 mL) under nitrogen atmosphere. This reaction mixture was stirred for 12 h at 80 °C. After cooling to room temperature, the solvent was evaporated. The resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate = 3:1 as eluent) to give compound **2** (30 mg, 77% isolated yield) as a green solid.

2: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 3.62 (s, 2 H), 4.08 (s, 2 H), 6.68 (d, J = 7.8 Hz, 1 H), 6.97 (t, J = 7.8 Hz, 1 H), 6.96-7.10 (m, 12 H), 7.09 (t, J = 7.8 Hz, 1 H), 7.17-7.20 (m, 7 H), 7.32-7.39 (m, 14 H), 7.67 (d, J = 8.4 Hz, 1 H), 7.89 (d, J = 7.8 Hz, 1 H), 8.33 (s, 1 H), 9.40 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 37.9, 41.4, 118.6, 124.7, 124.9, 125.4, 125.8, 125.9, 126.5, 126.9, 127.5, 127.9, 129.7, 129.9, 130.2 130.5, 130.7, 130.9, 131.2, 134.4, 134.9, 136.0, 136.4, 136.9, 137.0, 159.1. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 24.15. HRMS (FAB) calcd for $C_{58}H_{44}Br_2P_2Pd$: 1068.0322. Found: 1068.0358.

Preparation of palladated dihydropentacene 3.

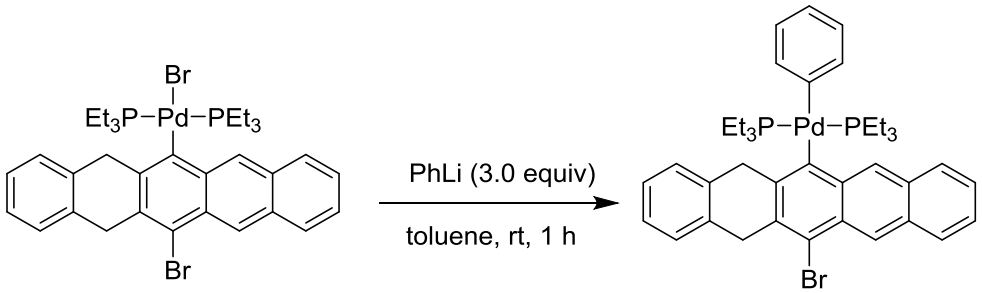


2 **3** 76%

In a 20 mL Schlenk tube, palladated dihydropentacene **2** (91 mg, 0.085 mmol) was dissolved in toluene (5 mL), and PEt_3 (0.36 mL, 0.34 mmol) was added at room temperature. Under nitrogen atmosphere, the mixture was stirred at 80 °C for 12 h. The solvent was evaporated to give a solid. Purification with a flash chromatography (silica gel, hexane: ethyl acetate = 5:1 as eluent) afforded the title compound **3** (50 mg, 76% isolated yield) as a green solid.

3 ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.94-1.02 (m, 18 H), 1.35-1.53 (m, 12 H), 4.34 (s, 2 H), 4.49 (s, 2 H), 7.23-7.25 (m, 2 H), 7.32-7.35 (m, 1 H), 7.41-7.44 (m, 1 H), 7.45-7.50 (m, 2 H), 7.93 (d, J = 7.2Hz, 1 H), 8.07 (d, J = 7.2 Hz, 1 H), 8.80 (s, 1 H), 9.37 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 8.4, 15.6, 38.3, 42.3, 118.9, 125.4, 125.4, 126.0, 126.4, 126.4, 126.6, 127.5, 127.6, 128.4, 130.3, 130.4, 131.4, 131.8, 134.4, 136.4, 137.2, 137.2, 137.5, 153.9. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 14.37. HRMS (FAB) calcd for $C_{34}H_{44}Br_2P_2Pd$: 780.0314. Found: 780.0302.

Preparation of palladated dihydropentacene 4 from 3



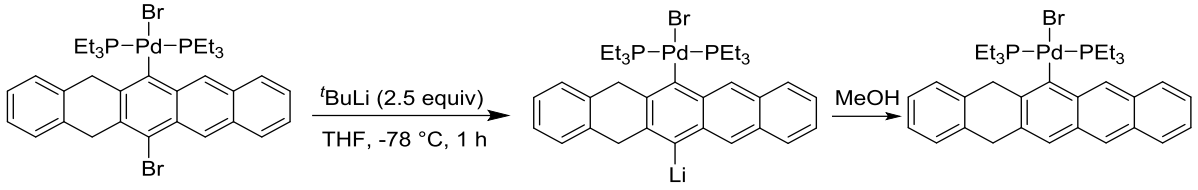
3 **4** 77%

In a 20 mL Schlenk tube, palladated dihydropentacene **3** (16 mg, 0.02 mmol) was dissolved in toluene (2 mL). After the solution was cooled to -78 °C, phenyllithium (0.042 mL, 0.06 mmol) was added dropwise. After which, remove the cooling bath, the mixture was then stirred for 1 h at room temperature. The mixture was quenched by addition with methanol. The solvent was evaporated, and

the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate =5:1 as eluent) to afford the title compound **4** (12 mg, 77% isolated yield).

4: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 0.90 (t, J = 7.8 Hz, 18 H), 1.00-1.05 (m, 6 H), 1.14-1.20 (m, 6 H), 4.08 (s, 2 H), 4.40 (s, 2 H), 4.52 (s, 2 H), 6.99 (t, J = 7.2 Hz, 2 H), 7.12-7.17 (m, 4 H), 7.22-7.24 (m, 4 H), 7.37-7.44 (m, 8 H), 7.76 (d, J = 7.2 Hz, 2 H),7.79 (d, J = 7.2 Hz, 2 H),7.96 (d, J = 7.8 Hz, 2 H), 8.08(d, J = 7.8 Hz, 2 H), 8.79 (s, 2 H), 9.44 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.4, 15.2, 38.7, 43.0, 118.5, 122.1, 124.4, 124.7, 125.4, 126.0, 126.1, 126.7, 126.8, 126.9, 127.6, 127.8, 128.6, 129.9, 130.7, 131.5, 133.1, 133.7, 137.3, 138.6, 138.7, 138.8, 139.7, 141.4, 168.0, 169.4. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 10.13. HRMS (ESI) calcd for $C_{40}H_{49}BrP_2Pd$: 776.1528. Found: 776.1523.

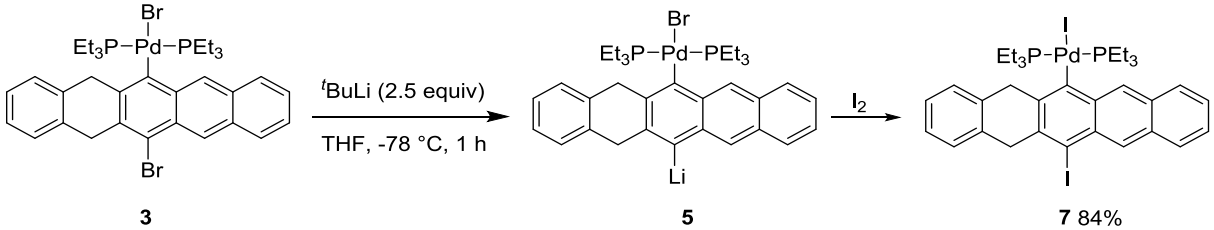
Preparation of palladated dihydropentacene 6



In a 20 mL Schlenk tube, palladated dihydropentacene **3** (60 mg, 0.0768 mmol) was dissolved in THF (2 mL). To the mixture was added ^{t}BuLi (0.109 mL, 0.192 mmol) at -78 °C, and it was stirred at -78 °C for 1 h to form **5**. After being quenched by methanol, the solvent was evaporated. The resulting solid was purified by a flash chromatography (silica gel, hexane: ethyl acetate =5:1 as eluent) to afford the title compound **6** (46 mg, 85% isolated yield).

6: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 0.95-1.00 (m, 18 H), 1.37-1.50 (m, 12 H), 4.08 (s, 2 H), 4.44 (s, 2 H), 7.21-7.23 (m, 2 H), 7.33-7.36 (m, 2 H), 7.37-7.43 (m, 2 H), 7.61 (s, 1 H), 7.92 (d, J = 7.8Hz, 1 H), 7.97 (d, J = 7.8 Hz, 1 H), 8.25 (s, 1 H), 9.28 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.5, 15.8, 38.1, 41.8, 121.3, 124.5, 124.9, 125.1, 126.3, 126.3, 127.0, 127.1, 127.9, 128.3, 130.4, 130.8, 131.3, 132.3, 135.3, 137.1, 137.6, 137.9, 153.1. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 14.19. HRMS (ESI) calcd for $C_{34}H_{45}BrP_2Pd$: 702.1219. Found: 702.1204.

Preparation of palladated dihydropentacene 7

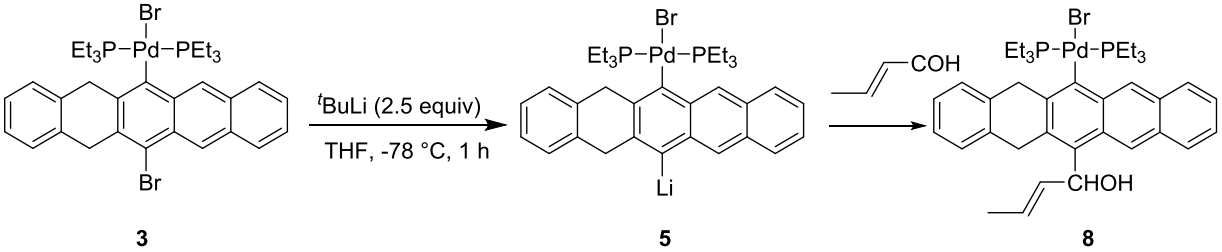


In a 20 mL Schlenk tube, a THF (2 mL) solution of palladated dihydropentacene **3** (68 mg, 0.087 mmol) cooled to -78 °C was added ^{t}BuLi (0.123 mL, 0.22 mmol). Under nitrogen atmosphere, the

mixture was stirred at -78 °C for 1 h. Iodine (67 mg, 0.262 mmol) was added to the mixture solution. After addition, remove the cooling bath, the mixture was stirred for 12 h at room temperature. The reaction solution was quenched by saturated aqueous $Na_2S_2O_3$ solution at 0 °C, extracted with ethyl acetate. The solvent was evaporated and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate =5:1 as eluent) to afford the title compound **7** (64 mg, 84% isolated yield).

7: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.93-0.98 (m, 18 H), 1.43-1.49 (m, 6 H), 1.54-1.61 (m, 6 H), 4.39 (s, 2 H), 4.45 (s, 2 H), 7.23-7.25 (m, 2 H), 7.32-7.33 (m, 1 H), 7.42-7.49 (m, 3 H), 7.91 (d, J = 7.8 Hz, 1 H), 8.09 (d, J = 8.4 Hz, 1 H), 8.75 (s, 1 H), 9.27 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 8.5, 16.8, 41.9, 44.9, 100.8, 125.4, 125.5, 126.4, 126.4, 126.5, 127.4, 128.3, 130.4, 131.0, 131.4, 132.1, 132.9, 136.8, 137.3, 137.4, 137.8, 139.2, 157.6. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 10.68. HRMS (ESI) calcd for $C_{34}H_{44}I_2P_2PdNa$: 892.9956[M + Na]$^+$. Found: 892.9951[M + Na]$^+$.

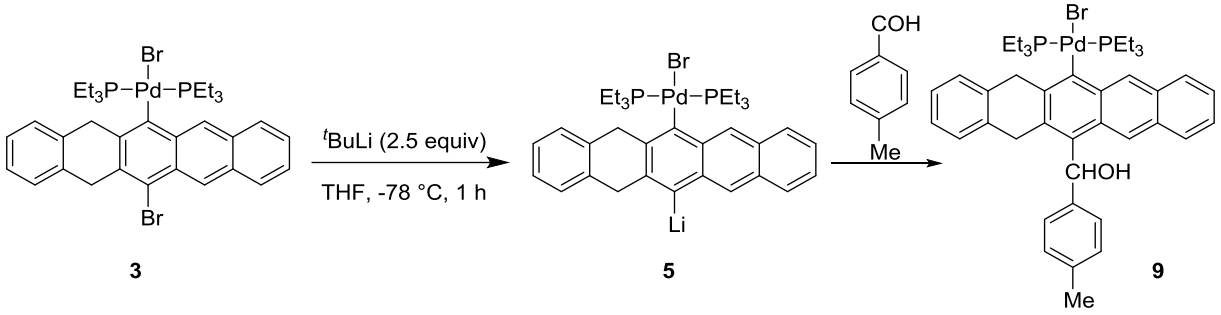
Preparation of palladated dihydropentacene 8 from 3



In a 20 mL Schlenk tube, palladated dihydropentacene **3** (22 mg, 0.028 mmol) was dissolved in THF (2 mL). To the mixture was added ^{t}BuLi (0.04 mL, 0.07 mmol) at -78 °C under a nitrogen atmosphere, and it was stirred at -78 °C for 1 h. Compound crotonaldehyde (0.005 mL, 0.056 mmol) was added to the mixture solution at -78 °C. After which, remove the cooling bath, the mixture was then stirred for 12 h at room temperature. The solution was quenched by methanol. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate =2:1 as eluent) to afford the title compound **8** (14 mg, 65% isolated yield).

8: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 0.93-1.00 (m, 18 H), 1.38-1.51 (m, 12 H), 1.69-1.7 (m, 3 H), 2.21 (s, 1 H), 4.16 (d, J = 16.8 Hz, 1 H), 4.34 (d, J = 16.8 Hz, 1 H), 4.39 (d, J = 16.2 Hz, 1 H), 4.59 (d, J = 16.2 Hz, 1 H), 5.60-5.64 (m, 1 H), 6.17-6.20 (m, 1 H), 6.46 (m, 1 H), 7.21-7.23 (m, 2 H), 7.33-7.35 (m, 2 H), 7.40-7.43 (m, 2 H), 7.89 (d, J = 9 Hz, 1 H), 7.99 (d, J = 9 Hz, 1 H), 8.86 (s, 1 H), 9.40 (s, 1 H). ^{13}C NMR (C_6D_6, Me_4Si, 600M) δ 8.5, 16.1, 17.8, 35.1, 42.8, 70.9, 123.7, 125.2, 125.3, 125.7, 126.5, 126.6, 126.8, 127.5, 129.1, 130.0, 130.4, 130.5, 131.7, 132.1, 134.4, 134.6, 138.1, 138.3, 138.8, 155.1. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 12.37. HRMS (FAB) calcd for $C_{38}H_{51}BrOP_2Pd$: 772.1635. Found: 772.1616.

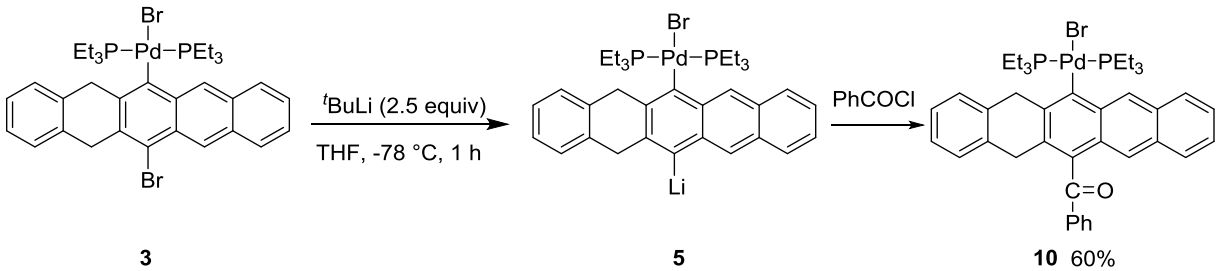
Preparation of palladated dihydropentacene 9 from 3



In a 20 mL Schlenk tube, palladated dihydropentacene **3** (21 mg, 0.027 mmol) was dissolved in diethyl ether : toluene (0.5 : 1.5) mL. To the mixture was added ^{t}BuLi (0.038 mL, 0.068 mmol) at -78 °C, and it was stirred at -78 °C for 1 h. *p*-Tolualdehyde (0.006 mL, 0.054 mmol) was added to the mixture solution at -78 °C. Remove the cooling bath, under nitrogen atmosphere, the mixture was stirred for 12 h at room temperature. After that the solution was quenched by methanol. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate =3:1 as eluent) to afford the title compound **9** (12.2 mg, 58% isolated yield).

9: ^{1}H NMR (C_6D_6, Me_4Si, 600M) δ 0.83-0.89 (m, 18 H), 1.29-1.44 (m, 12 H), 2.03 (br, 1 H), 2.13 (s, 3 H), 4.06 (d, J = 16.8 Hz, 1 H), 4.22 (d, J = 16.8 Hz, 1 H), 4.54 (d, J = 16.2 Hz, 1 H), 4.66 (d, J = 16.2 Hz, 1 H), 7.00 (s, 1 H), 7.07-7.10 (m, 3 H), 7.12-7.15 (m, 3 H), 7.25-7.28 (m, 1 H), 7.42 (d, J = 7.2 Hz, 1 H), 7.51 (d, J = 8.4 Hz, 2 H), 7.77 (d, J = 8.4 Hz, 1 H),8.05 (d, J = 8.4 Hz, 1 H), 8.94 (s, 1 H), 9.71 (s, 1 H). ^{13}C NMR (C_6D_6, Me_4Si, 600M) δ 8.6, 16.3, 21.1, 35.1, 42.8, 70.7, 124.0, 125.3, 125.4, 126.2, 126.5, 126.6, 126.7, 127.5, 129.2, 129.2, 130.5, 130.8, 130.9, 131.9, 132.1, 135.4, 136.0, 138.1, 138.2, 138.7, 142.4, 156.0. ^{31}P{^{1}H} NMR (C_6D_6, 600M) δ 12.54. HRMS (ESI) calcd for $C_{42}H_{53}BrONaP_2Pd$: 845.1686. Found: 845.1690.

Preparation of palladated dihydropentacene 10

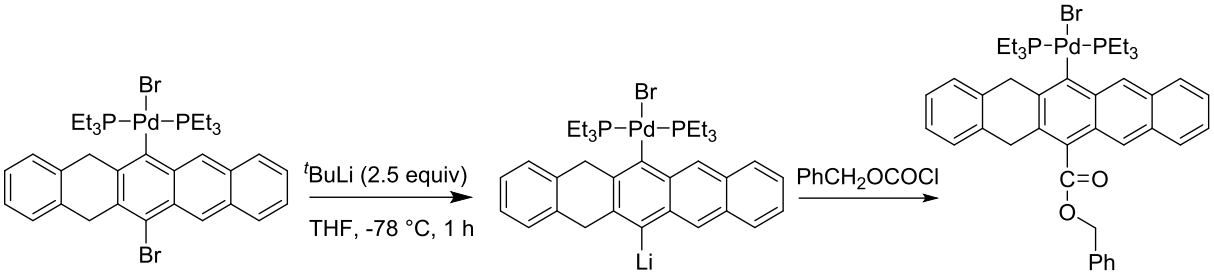


By the same method as described for compound **9** from palladated dihydropentacene **3**. Benzoyl chloride was used instead of *p*-tolualdehyde (2 equiv) to form the title compound **10** in 60% isolated yield.

10: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 1.00-1.05 (m, 18 H), 1.46-1.48 (m, 6 H), 1.54-1.56 (m, 6 H), 3.83 (s, 2 H), 4.52 (s, 2 H),7.03(d, J = 7.2 Hz, 1 H), 7.14 (t, J = 7.2 Hz, 1 H), 7.20(t, J = 7.2 Hz, 1

H),7.33-7.42 (m, 5 H), 7.57 (t, J = 7.2 Hz, 1 H), 7.78-7.79 (m, 3 H), 7.91(d, J = 8.4 Hz, 1 H), 8.00 (s, 1 H), 9.41 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.5, 15.8, 35.2, 41.8, 123.6, 125.1, 125.3, 126.3, 126.7, 127.1, 127.8, 128.1, 128.7, 128.8, 129.7, 130.0, 130.3, 131.4, 131.9, 133.7, 136.3, 136.5, 137.4, 138.3, 156.8, 200.8. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 12.62; HRMS (ESI) calcd for $C_{41}H_{49}BrOP_2PdNa$: 829.1373[M + Na]$^+$. Found: 829.1384[M + Na]$^+$.

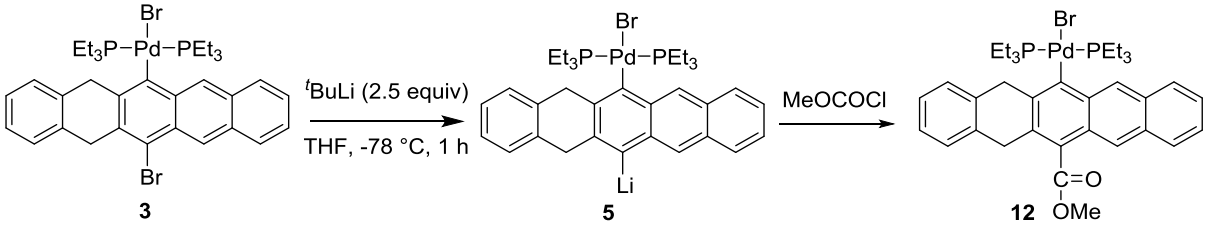
Preparation of palladated dihydropentacene 11



In a 20 mL Schlenk tube, under nitrogen atmosphere, palladated dihydropentacene **3** (17.6 mg, 0.0225 mmol) was dissolved in Et_2O: toluene (0.5 : 1.5) mL. To the mixture was added ^{t}BuLi (0.032 mL, 0.056 mmol) at -78 °C, and it was stirred at -78 °C for 1 h. Then benzyl chloroformate (0.004 mL, 0.027 mmol) was added to the mixture solution at -78 °C. The solution was warmed to room temperature and stirred for 12 h. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate =5:1 as eluent) to afford the title compound **11** (13 mg, 69% isolated yield) as a solid.

11: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 0.95-1.00 (m, 18 H), 1.36-1.40 (m, 6 H), 1.45-1.49 (m, 6 H), 4.00 (s, 2 H), 4.46 (s, 2 H), 5.65 (s, 2 H), 7.16-7.21 (m, 3 H), 7.30-7.31 (m, 1 H), 7.41-7.50 (m, 5 H), 7.64-7.65 (m, 2 H), 7.82-7.83 (m, 1 H), 7.88-7.90 (m, 1 H), 8.26 (s, 1 H), 9.36 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.4, 15.6, 35.4, 41.8, 67.1, 123.1, 124.3, 125.1, 125.3, 126.3, 126.6, 127.2, 127.7, 127.9, 128.2, 128.6, 128.8, 129.2, 130.2, 131.3, 131.5, 133.1, 136.0, 136.1, 136.3, 136.4, 137.3, 158.7, 170.3. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 12.42. HRMS (ESI) calcd for $C_{42}H_{52}BrOP_2Pd$: 837.1640[M + H]$^+$, Found: 837.1630[M + H]$^+$.

Preparation of palladated dihydropentacene 12

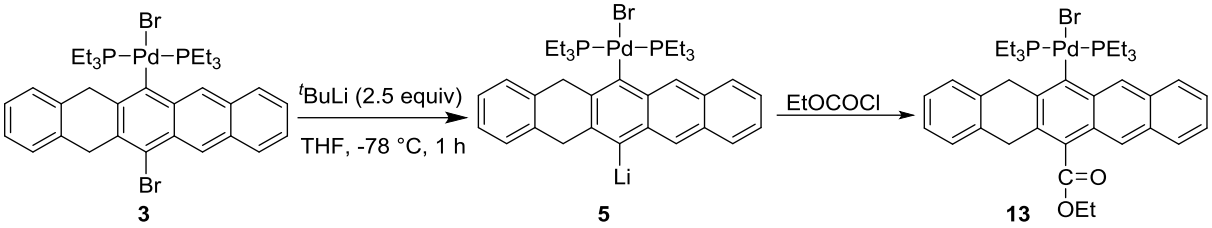


Compound **12** was synthesized by the same way as described for **11** from palladated dihydropentacene **3**. In this reaction methyl chloroformate was used. The title compound **12** was

obtained in 57% isolated yield.

12: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 0.98 (t, J = 7.8 Hz, 18 H), 1.37-1.42 (m, 6 H), 1.46-1.50 (m, 6 H), 4.08 (s, 2 H), 4.17 (s, 3 H), 4.49 (s, 2 H), 7.22-7.23 (m, 2 H), 7.33-7.34 (m, 2 H), 7.42-7.46 (m, 2 H), 7.90-7.91 (m, 1 H), 7.97-7.98 (m, 1 H), 8.32 (s, 1 H), 9.39 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.4, 15.6, 35.6, 41.8, 52.3, 123.1, 124.6, 125.1, 125.4, 126.3, 126.4, 126.6, 127.3, 127.8, 127.9, 128.2, 130.2, 131.4, 131.6, 133.1, 136.2, 136.3, 136.4, 137.3, 158.7, 171.0. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 12.44. HRMS (ESI) calcd for $C_{36}H_{47}BrO_2P_2PdNa$: 783.1166[M + Na]$^+$. Found: 783.1171[M + Na]$^+$.

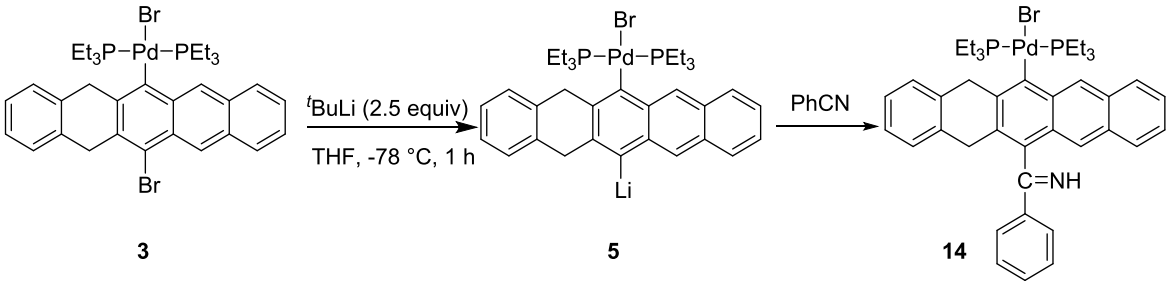
Preparation of palladated dihydropentacene 13



This compound was prepared by same method as described for **11** from complex **3**. Here, electrophilic reagent ethyl chloroformate was used in this reaction. Compound **13** was obtained in 68% isolated yield.

13: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 0.96-1.01 (m, 18 H), 1.36-1.42 (m, 6 H), 1.45-1.51 (m, 6 H), 1.58 (t, J = 7.2 Hz, 3 H), 4.10 (s, 2 H), 4.48 (s, 2 H), 4.68 (q, J = 7.2 Hz, 2 H), 7.22-7.24 (m, 2 H), 7.32-7.33 (m, 2 H), 7.41-7.45 (m, 2 H), 7.91 (d, J = 6.6 Hz, 1 H), 7.96 (d, J = 6.6 Hz, 1 H), 8.36 (s, 1 H), 9.38 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.4, 14.6, 15.6, 35.4, 41.8, 61.3, 123.1, 124.8, 125.1, 125.3, 126.3, 126.3, 126.6, 127.3, 127.8, 127.9, 128.2, 130.2, 131.4, 131.6, 132.9, 136.2, 136.3, 136.5, 137.3, 158.3, 170.5. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 12.45. HRMS (ESI) calcd for $C_{37}H_{49}BrO_2P_2PdNa$: 797.1322[M + Na]$^+$. Found: 797.1325[M + Na]$^+$.

Preparation of palladated dihydropentacene 14

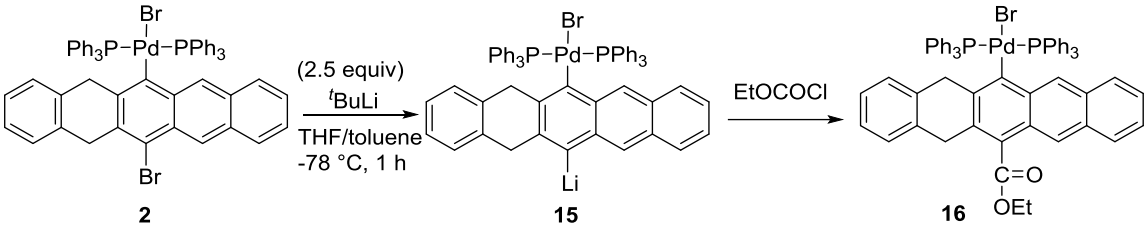


In a 20 mL Schlenk tube, palladated dihydropentacene **3** (22 mg, 0.028 mmol) was dissolved in THF (2 mL). To the mixture was added ^{t}BuLi (0.039 mL, 0.069 mmol) at -78 °C, and it was stirred at -78 °C for 1 h. Then benzonitrile (0.006 mL, 0.055 mmol) was added to the mixture solution at -78 °C and stirred for 2 h. After being quenched by methanol, the solvent was evaporated. The resulting

solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate =3:1 as eluent) to afford the title compound **14** (11 mg, 50% isolated yield).

14: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 0.96-0.1.07 (m, 18 H), 1.43-1.58 (m, 12 H), 3.74-3.96 (m, 2 H), 4.50-4.51 (m, 2 H), 7.09 (d, J = 7.2 Hz, 1 H), 7.15 (t, J = 7.2 Hz, 1 H), 7.21 (t, J = 7.2 Hz, 1 H), 7.30-7.34 (m, 3H), 7.36-7.44 (m, 3 H), 7.72-7.73 (m, 2 H), 7.81 (d, J = 8.4 Hz, 1 H), 7.91 (d, J = 8.4 Hz, 1 H), 8.09 (s, 1 H), 9.39 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.4, 8.5, 15.8 (q, J = 13 Hz), 35.2, 41.9, 123.8, 125.1, 125.2, 126.3, 126.6, 127.1, 127.8, 127.8, 128.1, 128.6, 128.9, 130.2, 131.1, 131.3, 131.4, 136.5, 136.6, 137.5, 138.6, 155.0, 178.3. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 12.65. HRMS (ESI) calcd for $C_{41}H_{50}BrNP_2Pd$: 805.1233 Found: 805.1210.

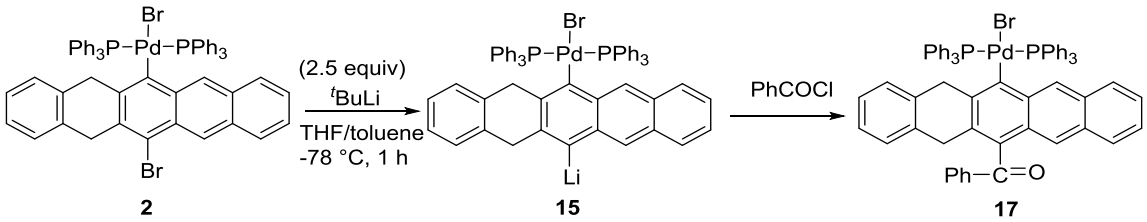
Preparation of palladated dihydropentacene 16



In a 20 mL Schlenk tube, under nitrogen atmosphere, palladated dihydropentacene **2** (25 mg, 0.023 mmol) was dissolved in THF : toluene (1 : 3) (2 mL). To the mixture was added ^{t}BuLi (0.033 mL, 0.058 mmol) at -78 °C, and it was stirred at -78 °C for 1 h. Then ethyl chloroformate (0.004 mL, 0.046 mmol) was added to the mixture solution at -78 °C. The mixture was warmed to room temperature and stirred for 12 h. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate: chloroform =5:1:1 as eluent) to afford the title compound **16** (14 mg, 57% isolated yield) as a pale yellow solid.

16: ^{1}H NMR ($CDCl_3$, Me_4Si, 400M) δ 1.51 (t, J = 7.2 Hz, 3 H), 3.32 (s, 2 H), 4.03 (s, 2 H), 4.55 (q, J = 7.2 Hz, 2 H), 6.64 (d, J = 7.6 Hz, 1 H), 6.94-7.08 (m, 16 H), 7.18-7.22 (m, 6 H), 7.29-7.37 (m, 13 H), 7.64 (d, J = 6.8 Hz, 1 H), 7.78 (d, J = 6.8 Hz, 1 H), 7.88 (s, 1 H), 9.39 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 400M) δ 14.5, 35.2, 40.8, 60.7, 122.4, 124.3, 124.8, 125.8, 125.9, 126.6, 126.6, 127.6, 127.7, 127.8, 129.7, 129.8, 130.4, 130.6, 130.9, 131.0, 132.9, 134.3, 135.4, 136.1, 137.1, 164.0, 170.1. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 24.3. HRMS (ESI) calcd for $C_{61}H_{49}BrO_2P_2Pd$: 1062.1406. Found: 1062.1410.

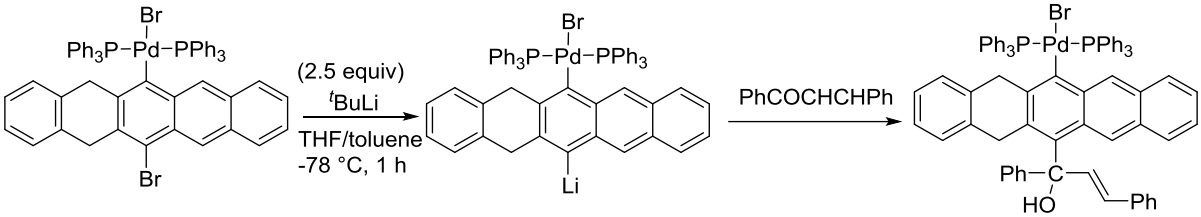
Preparation of palladated dihydropentacene 17



By the same method as described for **16**, the title compound **17** was obtained in 62% isolated yield as a pale yellow solid.

17: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 3.08 (s, 2 H), 4.15 (s, 2 H), 6.69 (d, J = 7.2 Hz,1 H), 6.75 (d, J = 7.2 Hz, 1 H), 6.95 (t, J = 7.2 Hz, 1 H), 6.98 (t, J = 7.2 Hz,1 H), 7.11-7.13 (m, 12 H), 7.23-7.28 (m, 10 H), 7.42-7.46 (m, 12 H), 7.57 (s, 1 H), 7.59-7.60 (m, 2 H),7.63 (d, J = 7.8 Hz, 1 H), 7.74-7.76 (m, 2 H), 9.49 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 35.1, 41.2, 123.1, 124.3, 124.6, 125.7, 125.8, 126.4, 126.6, 127.8, 128.4, 128.9, 129.7, 130.0, 130.8, 132.7, 133.5, 134.4, 135.7, 135.8, 136.2, 137.5, 138.3, 159.3, 200.2. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 24.6. HRMS (FAB) calcd for $C_{65}H_{49}BrOP_2Pd$: 1094.1487. Found: 1094.1504.

Preparation of palladated dihydropentacene 18

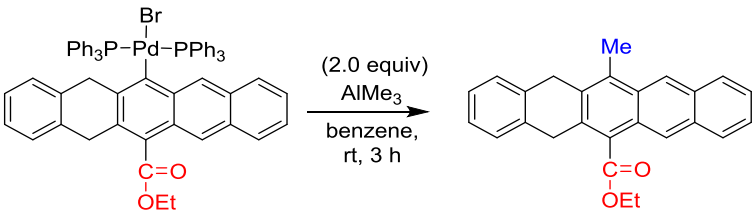


2 **15** **18**

In a 20 mL Schlenk tube, under nitrogen atmosphere, palladated dihydropentacene **2** (62 mg, 0.058 mmol) was dissolved in THF (4 mL). To the mixture was added ^{t}BuLi (0.082 mL, 0.145 mmol) at -78 °C, and it was stirred for 1 h. Reagent (E)-chalcone (14 mg, 0.07 mmol) was added to the mixture solution at -78 °C. The mixture was warmed to room temperature and stirred for 12 h. The reaction mixture was quenched with methanol. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate: chloroform =3:1:1 as eluent) to afford the title compound **18** (46 mg, 66% isolated yield) as a yellow solid.

18: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 2.27 (s, 1 H), 3.35 (d, J = 15.6 Hz, 1 H), 3.62 (d, J = 15.6 Hz, 1 H), 4.13 (d, J = 15.6 Hz, 1 H), 4.42 (d, J = 15.6 Hz, 1 H), 6.03 (d, J = 15.6 Hz, 1 H), 6.48 (d, J = 7.2 Hz, 1 H), 6.60 (d, J = 7.8 Hz, 1 H), 6.70 (d, J = 15.6 Hz, 1 H), 6.85 (t, J = 7.2 Hz, 1 H), 6.91 (t, J = 7.8 Hz, 1 H), 7.06-7.11 (m, 12 H), 7.18-7.52 (m, 31 H), 7.68 (d, J = 8.4 Hz, 1 H), 8.41 (s, 1 H), 9.58 (s, 1 H). ^{31}P{^{1}H} NMR ($CDCl_3$) δ 24.3. HRMS (FAB) calcd for $C_{73}H_{57}BrOP_2Pd$: 1198.2116. Found: 1198.2139.

Preparation of palladated dihydropentacene 19

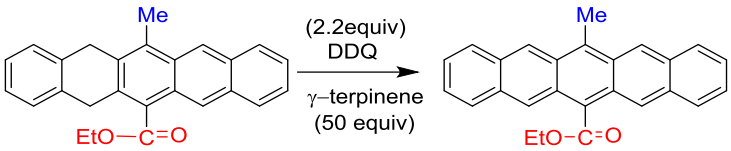


16 **19** 95%

In a 20 mL Schlenk tube, palladated dihydropentacene **16** (30 mg, 0.0282 mmol) was dissolved in benzene (2 mL). To the mixture was added $AlMe_3$ (0.052 mL, 0.056 mmol) at room temperature, and it was stirred for 3 h at room temperature. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate = 5:1 as eluent) to afford the title compound **19** (9.9 mg, 95% isolated yield).

19: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 1.56 (t, J = 7.2 Hz, 3 H), 2.91 (s, 3 H), 4.11 (s, 2 H), 4.20 (s, 2 H), 4.68 (q, J = 7.2 Hz, 2 H), 7.23-7.25 (m, 2 H), 7.33 (t, J = 4.2 Hz, 1 H), 7.38 (t, J = 4.2 Hz, 1 H), 7.45-7.47 (m, 2 H), 7.96-7.97 (m, 1 H), 8.01-8.03 (m, 1 H), 8.34 (s, 1 H), 8.62 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 14.5, 15.3, 33.9, 35.1, 61.5, 123.1, 123.6, 125.5, 125.6, 126.5, 126.6, 126.9, 127.2, 127.2, 127.3, 128.1, 128.4, 130.0, 131.4, 131.4, 132.0, 133.0, 136.1, 136.6, 170.1. HRMS (EI) calcd for $C_{26}H_{22}O_2$: 366.1620. Found: 366.1614.

Preparation of palladated pentacene 20



19 **20** 42%

In a 20 mL Schlenk tube, palladated dihydropentacene **19** (9.9 mg, 0.027 mmol) and 2,3-dichloro-5,6-dicyanobenzoquinone (13.5 mg, 0.059 mmol) were dissolved in benzene (2 mL). Under nitrogen atmosphere, the mixture was stirred for 2 h at 50 °C. The pentacene-DDQ adduct was formed firstly, without isolation of pentacene-DDQ adduct, γ-terpinene (0.22 mL, 1.35 mmol) was added to the reaction solution. The mixture was degassed by three times of freeze-pump thaw cycle and heated at 80 °C for about 6 h. After cooling to room temperature, the solvent was removed in vacuo. The resulting solids were purified by a flash chromatography (silica gel, $CHCl_3$ as eluent) under nitrogen to afford the title compound **20** (4.1mg, 42% isolated yield) as a blue solid.

20: ^{1}H NMR ($CDCl_3$, Me_4Si, 400M) δ 1.64 (t, J = 7.2 Hz, 3 H), 3.48 (s, 3 H), 4.85 (q, J = 7.2 Hz, 2 H), 7.26-7.39 (m, 4 H), 7.90-7.92 (m, 2 H), 7.96-7.98 (m, 2 H), 8.66 (s, 2 H), 8.96 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 400M) δ 14.6, 15.4, 61.9, 123.8, 123.9, 125.5, 125.9, 126.3, 127.8, 128.3, 128.7, 131.1, 131.8, 133.8, 170.7. HRMS (EI) calcd for $C_{26}H_{20}O_2$: 364.1463. Found: 364.1468

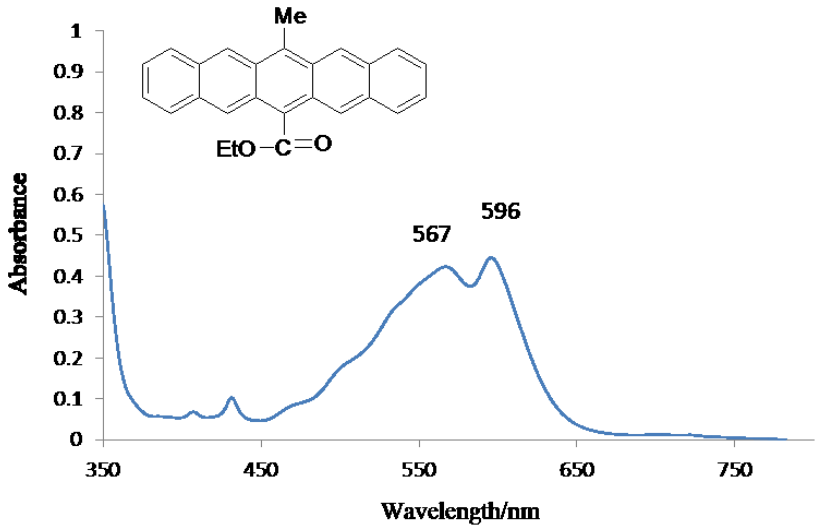
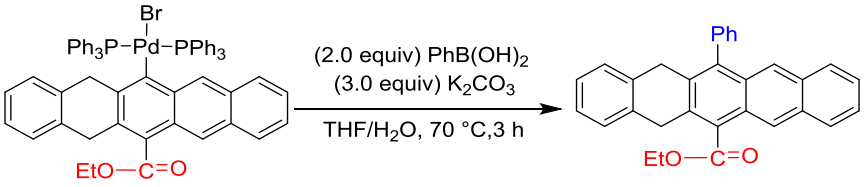


Figure S1. Absorption spectrum of pentacene derivative **20** in CH_2Cl_2 at rt.

Preparation of palladated dihydropentacene 21

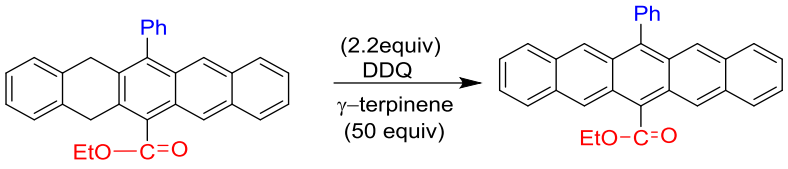


16 **21** 88%

In a 20 mL Schlenk tube, palladated dihydropentacene **16** (43 mg, 0.04 mmol), phenylboronic acid (10 mg, 0.08 mmol) and potassium carbonate (17 mg, 0.12 mmol) were dissolved in mixed solution of THF and H_2O (10:1) (2 mL). The solution was degassed by three times of freeze-pump-thaw cycles and heated at 70 °C for 3 h. The solvent was evaporated, and the resulting solids were purified by column chromatography (silica gel, hexane: ethyl acetate = 5:1 as eluent) to afford the title compound **21** (15 mg, 88% isolated yield) as solid.

21: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 1.59 (t, J = 7.6 Hz, 3 H), 3.81 (s, 2 H), 4.17 (s, 2 H), 4.73 (q, J = 7.6 Hz, 2 H), 7.11-7.24 (m, 3 H), 7.33-7.45 (m, 5 H), 7.56-7.64 (m, 3 H), 7.78 (d, J = 8.4 Hz, 1 H), 7.94 (s, 2 H), 7.97 (d, J = 8.4 Hz, 1 H), 8.42 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 400M) δ 14.6, 34.9, 35.2, 61.6, 123.1, 125.4, 125.7, 125.8, 126.5, 126.8, 127.1, 127.2, 127.7, 128.1, 128.4, 128.7, 130.2, 131.3, 131.5, 132.5, 133.3, 136.1, 136.9, 138.2, 139.0, 169.9. HRMS (EI) calcd for $C_{31}H_{24}O_2$: 428.1776. Found: 428.1773.

Preparation of palladated pentacene 22



21 **22** 85%

By the same aromatic method as described for pentacene **20**, the title compound **22** was obtained in 85% isolated yield as a blue solid.

22: ^{1}H NMR ($CDCl_3$, Me_4Si, 400M) δ 1.67 (t, J = 7.2 Hz, 3 H), 4.89 (q, J = 7.2 Hz, 2 H), 7.25-7.29 (m, 2 H), 7.33-7.37 (m, 2 H), 7.55-7.57 (m, 2 H), 7.68-7.74 (m, 5 H), 7.92 (d, J = 8.8 Hz, 2 H), 8.29 (s, 2 H), 8.70 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 14.6, 62.1, 123.3, 125.4, 126.1, 126.2, 126.3, 127.5, 128.0, 128.2, 128.3, 128.6, 128.7, 131.1, 131.4, 132.0, 138.9, 140.1, 170.5. HRMS (EI) calcd for $C_{31}H_{22}O_2$: 426.1620. Found: 426.1625.

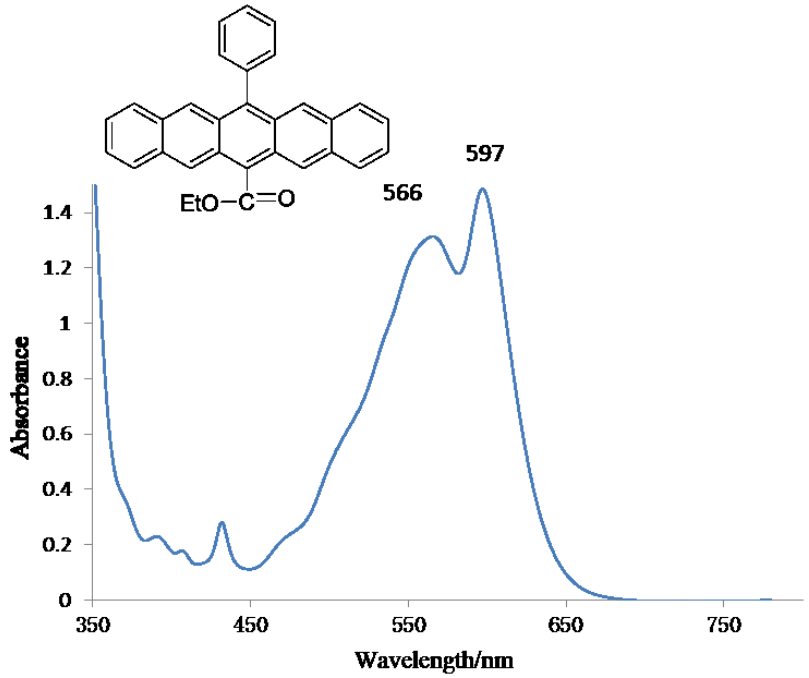
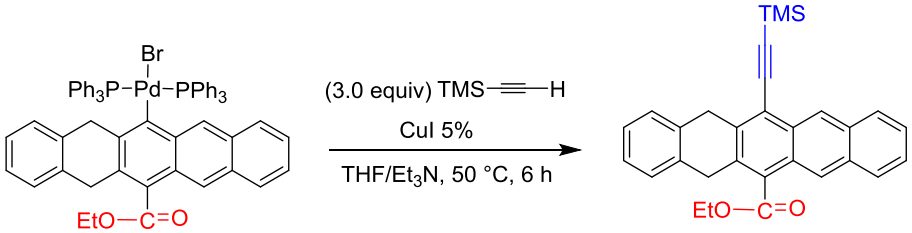


Figure S2. Absorption spectrum of pentacene derivative **22** in $CHCl_3$ at rt.

Preparation of palladated dihydropentacene 23

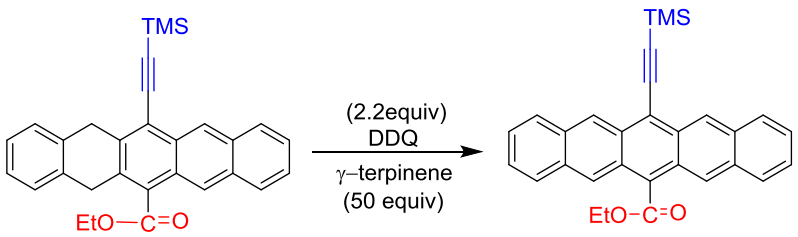


16 **23** 86%

In a 20 mL Schlenk tube, palladated dihydropentacene **16** (13.7 mg, 0.0129 mmol) and CuI (3 mg, 0.016 mmol) were dissolved in mixed solution of THF : Et_3N (1 : 1) (2 mL). The mixture was degassed by three times of freeze-pump thaw cycle. To the mixture was added trimethylsilylacetylene (0.005 mL, 0.039 mmol) at room temperature, and it was stirred for 6 h at 50 °C. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate = 5:1 as eluent) to afford the title compound **23** (5 mg, 86% isolated yield) as a solid.

23: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 0.47 (s, 9 H), 1.57 (t, J = 7.2 Hz, 3 H), 4.11 (s, 2 H), 4.41 (s, 2 H), 4.69 (q, J = 7.2 Hz, 2 H), 7.23-7.28 (m, 2 H), 7.33 (d, J = 7.2 Hz, 1 H), 7.40 (d, J = 7.2 Hz, 1 H), 7.47-7.51 (m, 2 H), 7.98 (d, J = 8.4 Hz, 1 H), 8.05 (d, J = 8.4 Hz, 1 H), 8.38 (s, 1 H), 8.92 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 400M) δ 0.2, 14.5, 34.7, 35.7, 61.7, 101.4, 106.4, 119.5, 123.7, 125.4, 125.9, 126.4, 126.6, 126.7, 127.3, 127.5, 128.3, 128.4, 129.0, 129.7, 131.8, 131.9, 132.8, 135.6, 136.0, 138.8, 169.4. HRMS (EI) calcd for $C_{30}H_{28}O_2Si$: 448.1859. Found: 448.1862.

Preparation of palladated pentacene 24



23 **24** 88%

In a 20 mL Schlenk tube, palladated dihydropentacene **23** (6.2 mg, 0.0138 mmol) and 2,3-dichloro-5,6-dicyanobenzoquinone (7 mg, 0.0304 mmol) were dissolved in benzene (2 mL). Under nitrogen atmosphere, the mixture was stirred for 1 h at room temperature. The pentacene-DDQ adduct was formed firstly. Without isolation of pentacene-DDQ adduct, γ-terpinene (0.11 mL, 0.69 mmol) was added to the reaction solution. The mixture was degassed by three times of freeze-pump thaw cycle and heated at 80 °C for about 1 h. After cooling to room temperature, the solvent was removed in vacuo. The resulting solids were purified by a flash chromatography (silica gel, $CHCl_3$ as eluent) under nitrogen to afford the title compound **24** (4.7 mg, 88% isolated yield) as a blue solid.

24: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 0.55 (s, 9 H), 1.64 (t, J = 7.2Hz, 3 H), 4.86 (t, J = 7.2Hz, 2 H), 7.38-7.42 (m, 4 H), 7.93-7.94 (m, 2 H), 8.01-8.03 (m, 2 H), 8.65 (s, 2 H), 9.24 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 0.3, 14.6, 62.2, 102.4, 110.4, 119.7, 124.1, 126.0, 126.1, 126.1, 126.2, 128.5, 128.7, 130.2, 132.0, 132.3, 169.9. HRMS (EI) calcd for $C_{30}H_{26}O_2Si$: 446.1702. Found: 446.1697.

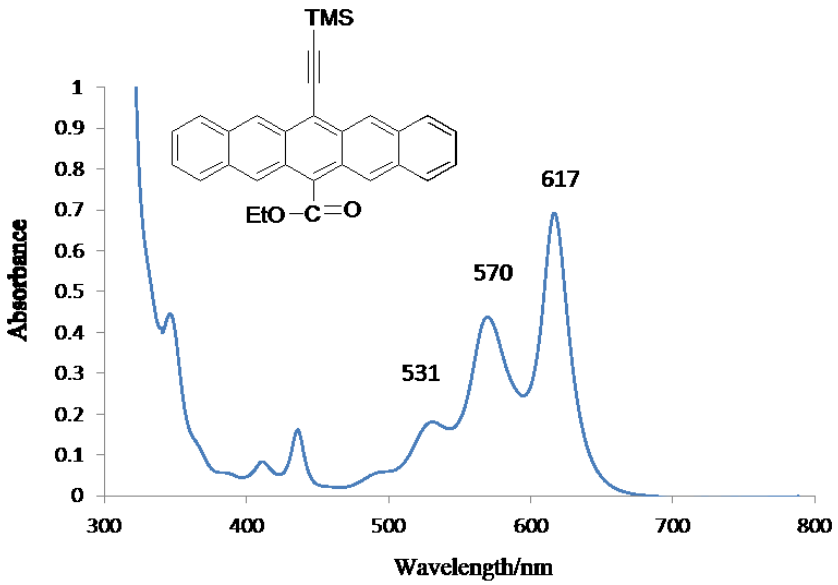


Figure S3. Absorption spectrum of pentacene derivative **24** in $CHCl_3$ at rt.

References

1. a) Z. Jia, S. Li, K. Nakajima, K. Kanno and T. Takahashi, *J. Org. Chem.* 2011, **76**, 293-296. b) Z. Jia, S. Li, K. Nakajima, K. Kanno, Z. Song and T. Takahashi, *Heterocycles* 2012, **86**, 1495-1506.
2. D. R. Coulson, L. C. Satek and S. O. Grim, *Inorg. Synth.* 1972, **13**, 121.

X-ray analysis data for compound 2

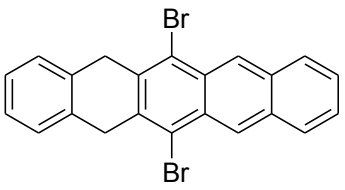
Table 1. Crystallographic data and experimental details

Compound	**2**
Formula	C_{58} H_{44} Br_2 P_2 Pd
M	1069.09
Crystal system	monoclinic
Space group	P 1 21/c 1
a, (Å)	11.581(3)
b, (Å)	18.509(4)
c, (Å)	22.700(5)
α, (°)	90.00
β, (°)	100.345(11)
γ, (°)	90.00
V, (Å^3)	4787(2)
Z	4
Temperature T, (K)	298
Crystal habit	prism
Crystal color	Green
Crystal size, (mm^3)	0.60 x 0.30 x 0.10
D_{calcd}, (g cm^{-3})	1.483
Transm factor	0.3570-0.8128
λ (Mo Kα), (Å^3)	0.71075
Diffractometer	Rigaku R-AXIS RAPID
Scan mode	ω
Reflections measd	-15≤ h ≤ 15
	-24≤ k ≤ 24
	-29≤ l ≤ 29
No. of reflection measd	10898
No. of reflection obsd [I>2σ(I)]	8373
No. of parameters refined	744
R	0.0495
R_ω	0.1342
S, goodness of fit	1.020
Largest diff peak, (e Å^{-3})	1.393
Largest diff hole, (e Å^{-3})	-0.982

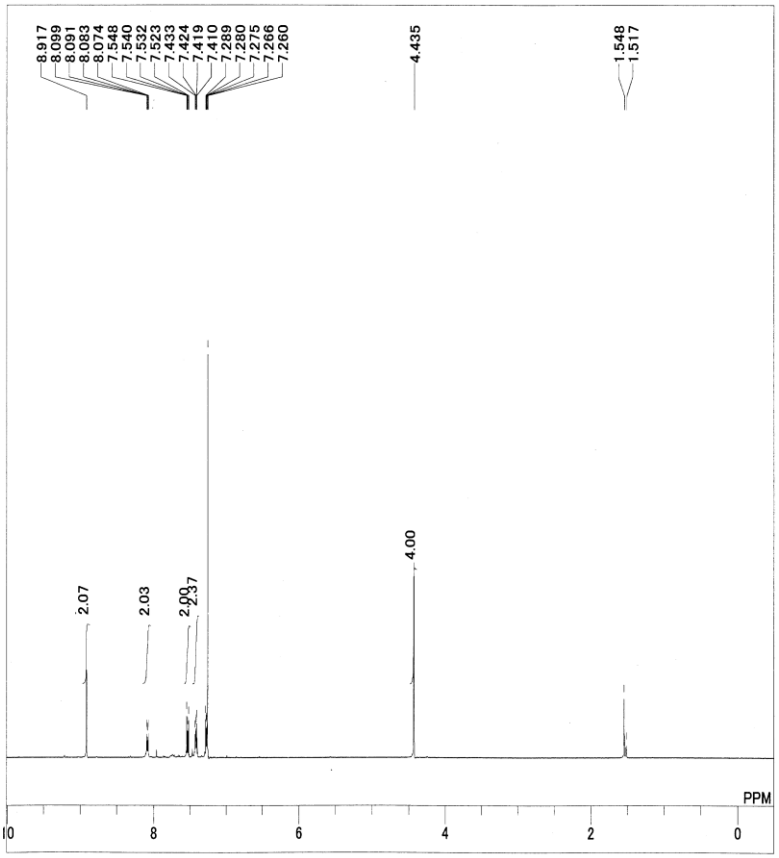
$R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$,

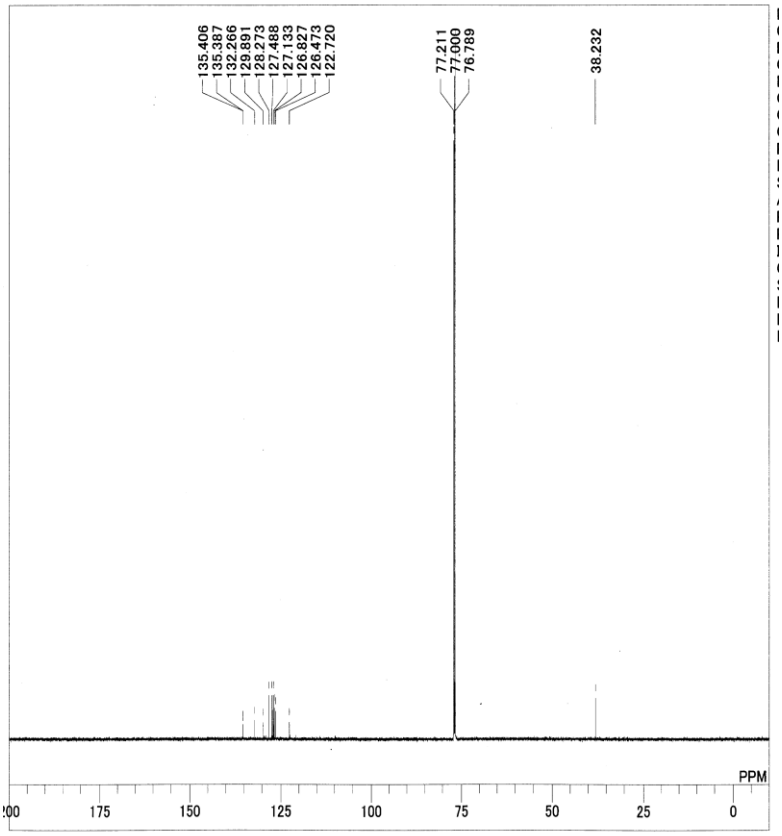
$R_\omega=[\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$, $\omega=[\sigma^2(F_o)+0.00063(F_o)^2]^{-1}$.

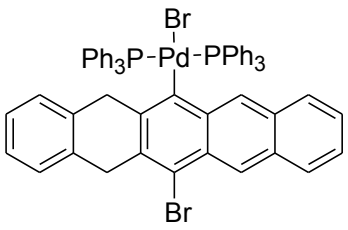
$S=[\Sigma\omega(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, (m=no. of used reflections, n=no. of refined parameters)


Br
Br

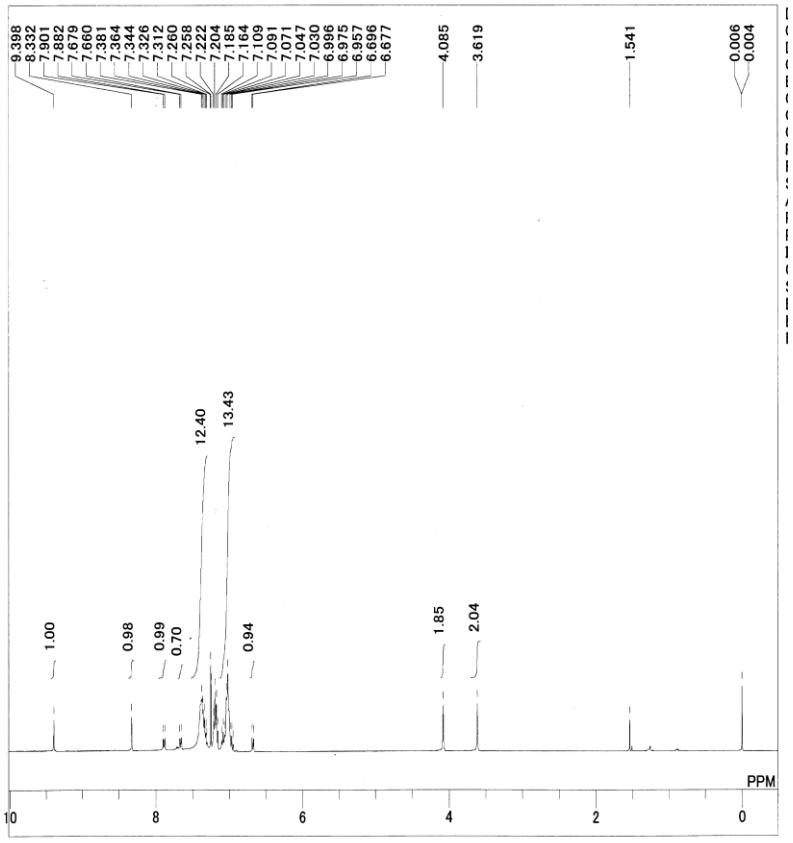
1

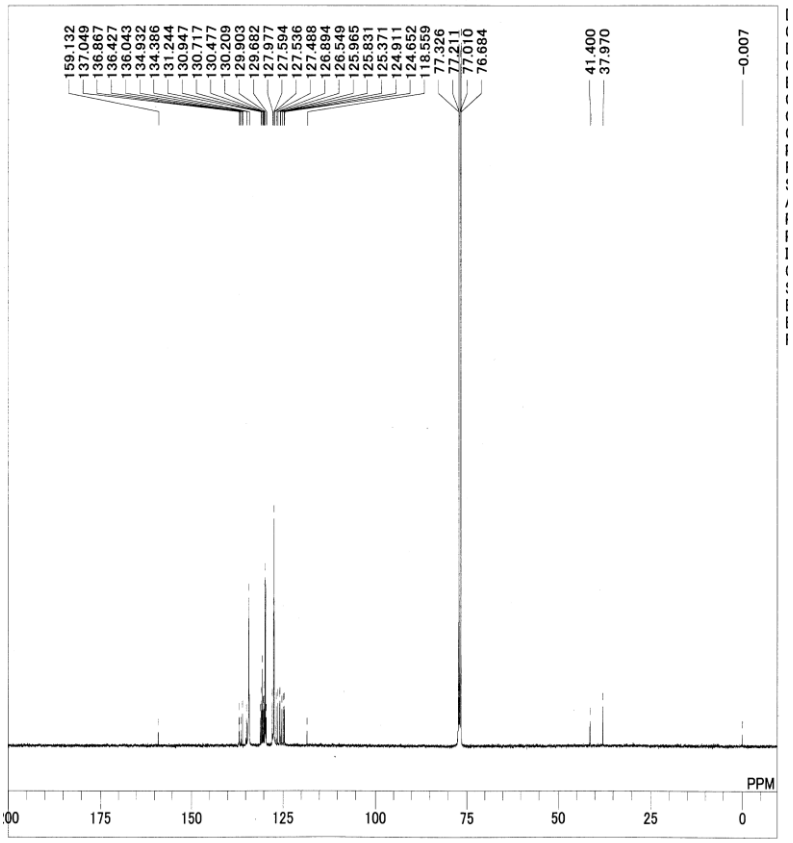

8.917
8.099
8.091
8.083
8.074
7.548
7.540
7.532
7.523
7.433
7.424
7.419
7.410
7.289
7.280
7.275
7.266
7.260
4.435
1.548
1.517
2.07
2.03
2.00
2.37
4.00
PPM
10
8
6
4
2
0

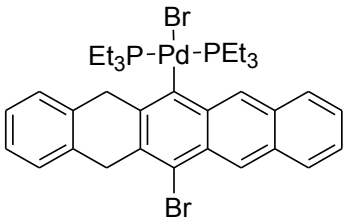

135.406
135.387
132.266
129.891
128.273
127.488
127.133
126.827
126.473
122.720
77.211
77.000
76.789
38.232
PPM
200
175
150
125
100
75
50
25
0


Br
Ph3P-Pd-PPh3
Br

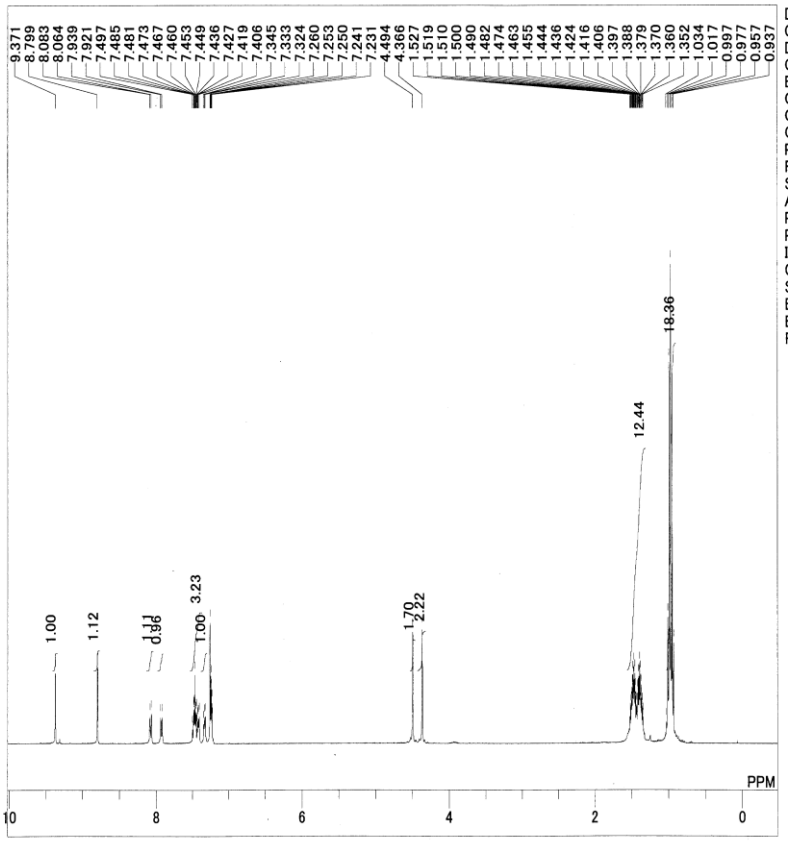
2

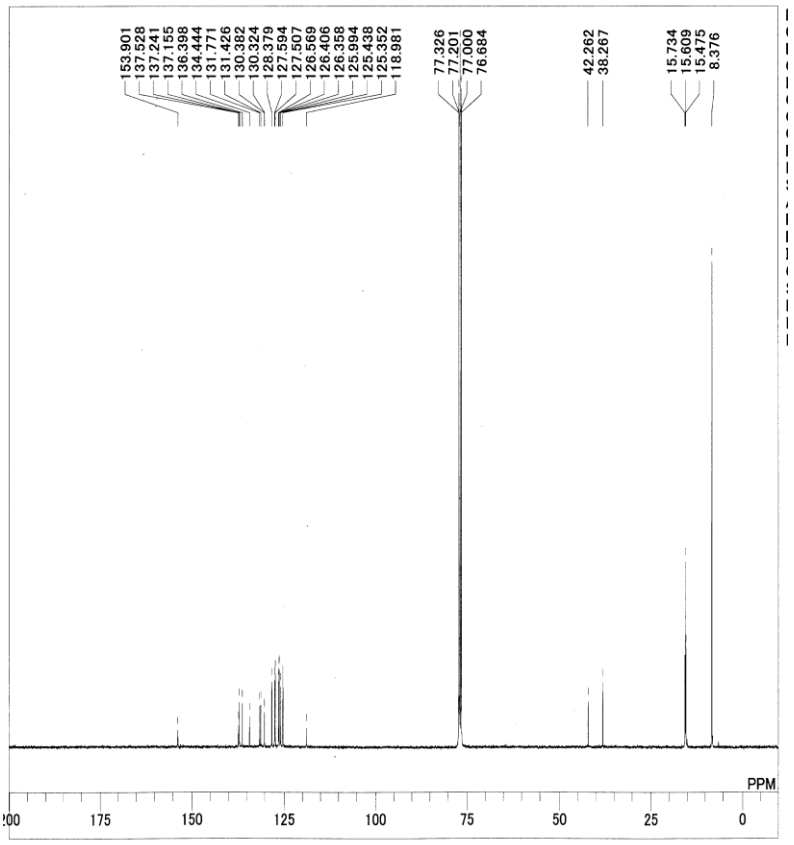

9.398
8.332
7.901
7.882
7.679
7.660
7.381
7.364
7.344
7.326
7.312
7.260
7.258
7.222
7.204
7.185
7.164
7.109
7.091
7.071
7.047
7.030
6.996
6.975
6.957
6.696
6.677
4.085
3.619
1.541
0.006
0.004
12.40
13.43
1.00
0.98
0.99
0.70
0.94
1.85
2.04
PPM
10
8
6
4
2
0

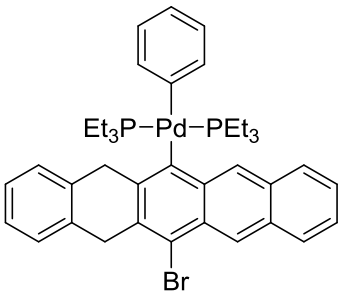

159.132
137.049
136.867
136.427
136.043
134.932
134.386
131.244
130.947
130.717
130.477
130.209
129.903
129.682
127.977
127.594
127.536
127.488
126.894
126.549
125.965
125.831
125.371
124.911
124.652
119.559
77.326
77.211
77.010
76.684
41.400
37.970
-0.007
PPM
200
175
150
125
100
75
50
25
0


Br
Et3P-Pd-PEt3
Br

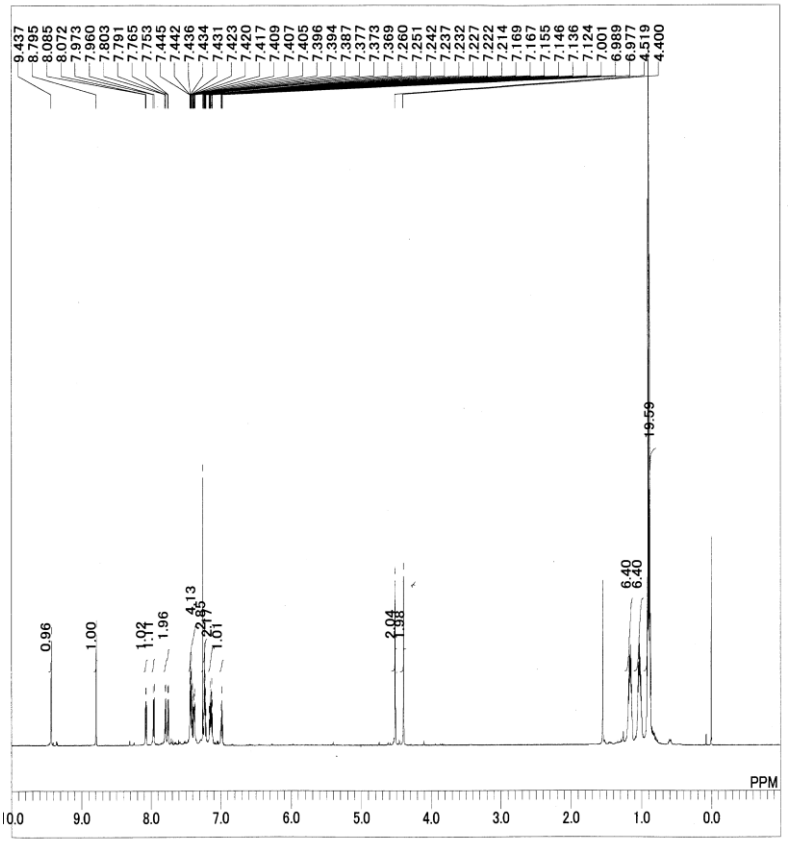
3

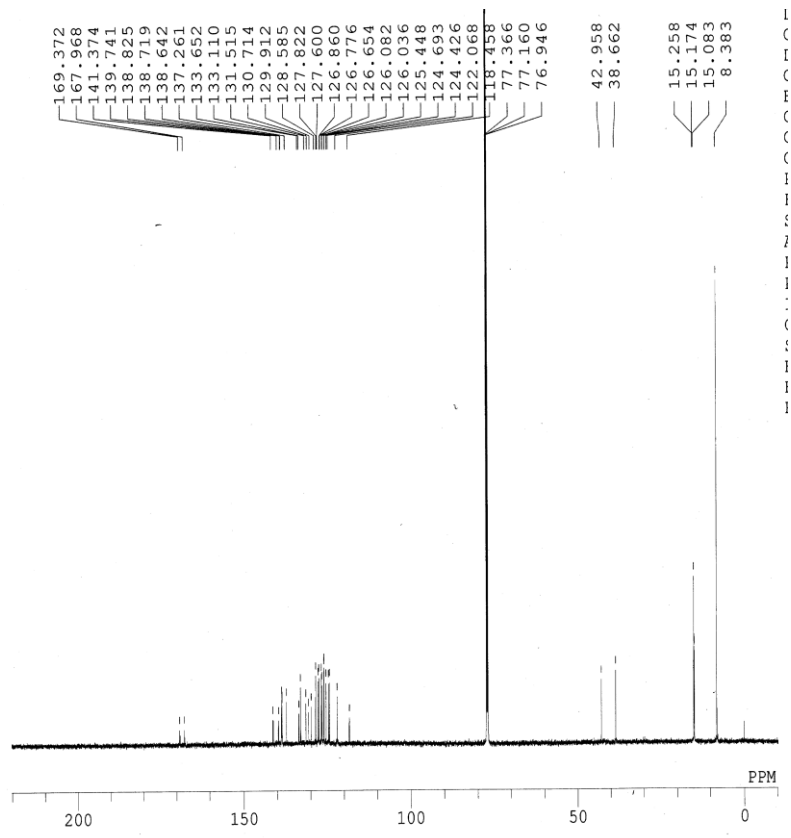

9.371
8.799
8.083
8.064
7.939
7.921
7.497
7.485
7.481
7.473
7.467
7.460
7.453
7.449
7.436
7.427
7.419
7.406
7.345
7.333
7.324
7.260
7.253
7.250
7.241
7.231
4.494
4.366
1.527
1.519
1.510
1.500
1.490
1.482
1.474
1.463
1.455
1.444
1.436
1.424
1.416
1.406
1.397
1.388
1.379
1.370
1.360
1.352
1.034
1.017
0.997
0.977
0.957
0.937
18.36
12.44
1.70
2.22
3.23
1.00
1.00
1.12
1.00
PPM
10
8
6
4
2
0

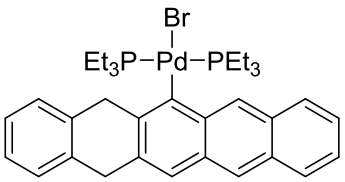

153.901
137.528
137.241
137.155
136.398
134.444
131.771
131.426
130.382
130.324
128.379
127.594
127.507
126.569
126.406
126.358
125.994
125.438
125.352
118.981
77.326
77.201
77.000
76.684
42.262
38.267
15.734
15.609
15.475
8.376
PPM
175
150
125
100
75
50
25
0


Et3P−Pd−PEt3
Br

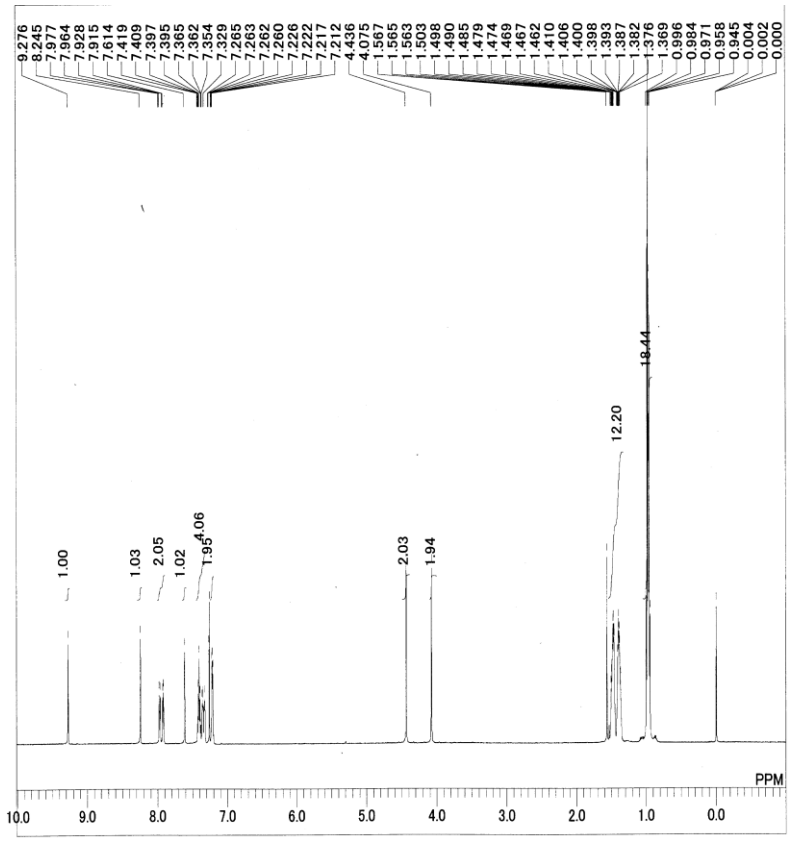
4

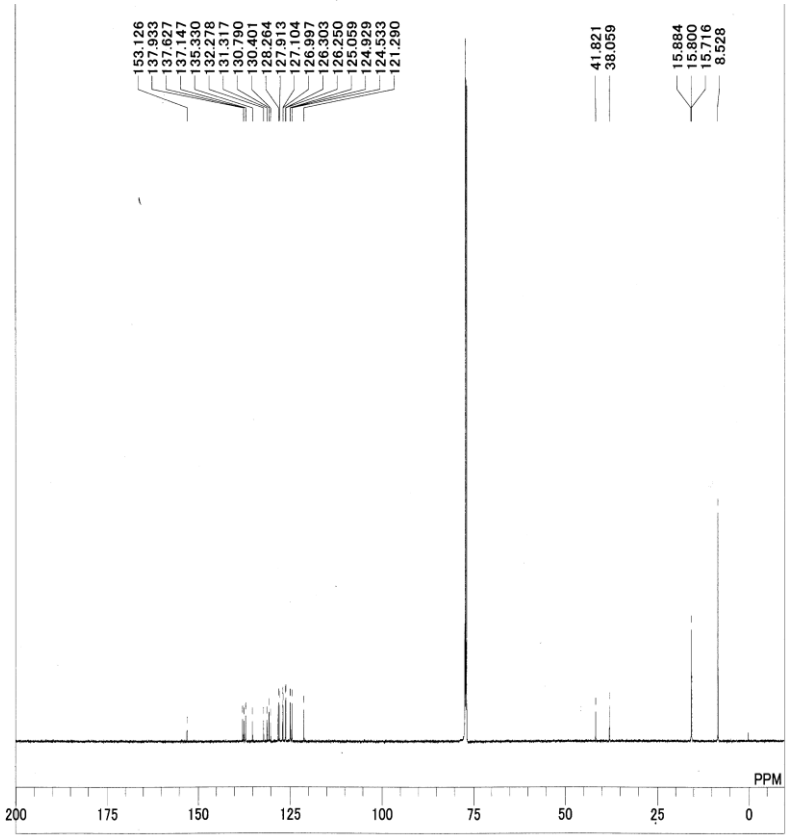

9.437
8.795
8.085
8.072
7.973
7.960
7.803
7.791
7.765
7.753
7.445
7.442
7.436
7.434
7.431
7.423
7.420
7.417
7.409
7.407
7.405
7.396
7.394
7.387
7.377
7.373
7.369
7.260
7.251
7.242
7.237
7.232
7.227
7.222
7.214
7.169
7.167
7.155
7.146
7.136
7.124
7.001
6.989
6.977
4.519
4.400
19.59
6.40
6.40
0.96
1.00
1.02
1.17
1.96
2.13
2.03
2.15
1.61
2.04
1.98
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

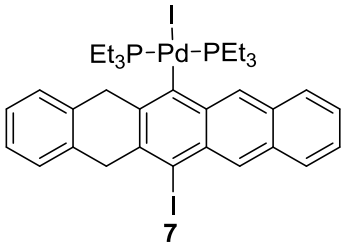

169.372
167.968
141.374
139.741
138.825
138.719
138.642
137.261
133.652
133.110
131.515
130.714
129.912
128.585
127.822
127.600
126.860
126.776
126.654
126.082
126.036
125.448
124.693
124.426
122.068
118.458
77.366
77.160
76.946
42.958
38.662
15.258
15.174
15.083
8.383
PPM
200
150
100
50
0


Br
Et3P–Pd–PEt3

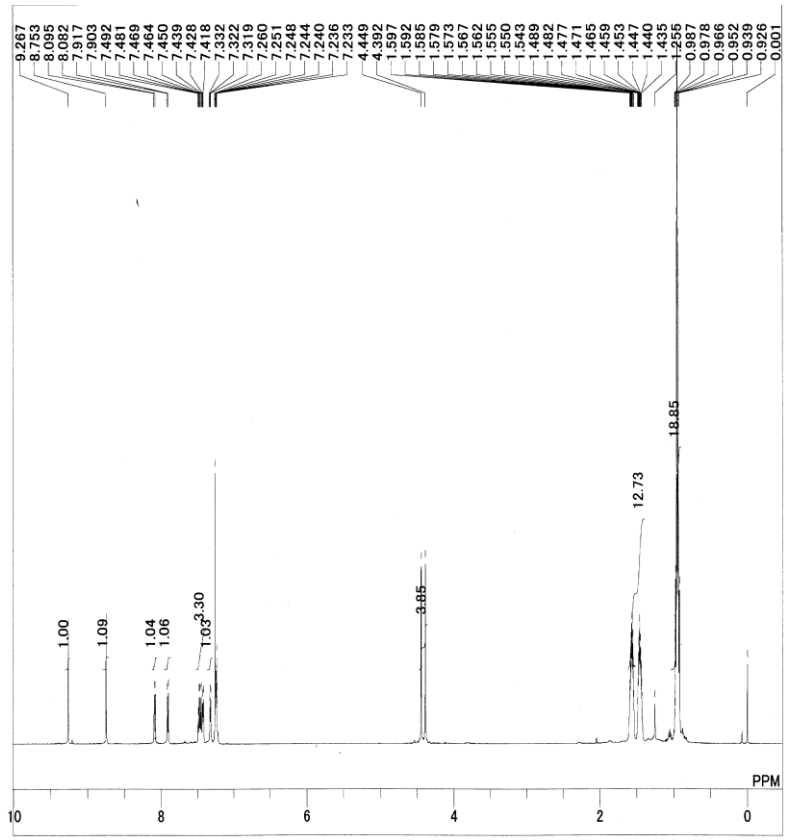
6

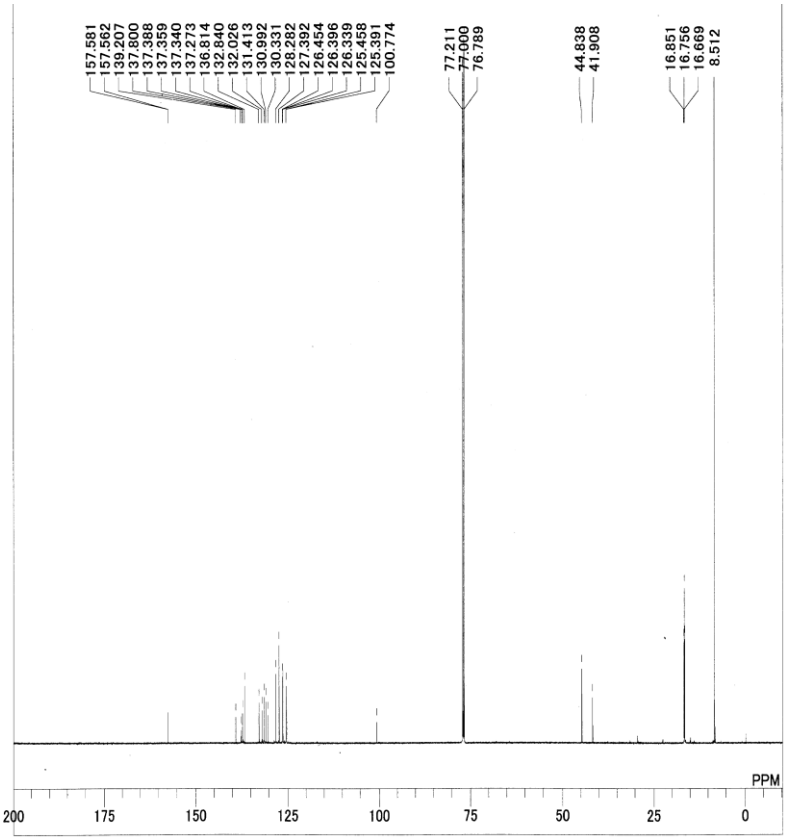

9.276
8.245
7.977
7.964
7.928
7.915
7.614
7.419
7.409
7.397
7.395
7.365
7.362
7.354
7.329
7.265
7.263
7.262
7.260
7.226
7.222
7.217
7.212
4.436
4.075
1.567
1.565
1.563
1.503
1.498
1.490
1.485
1.479
1.474
1.469
1.467
1.462
1.410
1.406
1.400
1.398
1.393
1.387
1.382
1.376
1.369
0.996
0.984
0.971
0.958
0.945
0.004
0.002
0.000
18.44
12.20
4.06
2.05
2.03
1.94
1.03
1.02
1.00
1.95
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

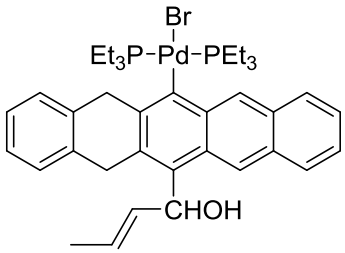

153.126
137.933
137.627
137.147
135.330
132.278
131.317
130.790
130.401
128.264
127.913
127.104
126.997
126.303
126.250
125.059
124.929
124.533
121.290
41.821
38.059
15.884
15.800
15.716
8.528
PPM
200
175
150
125
100
75
50
25
0


Et3P-Pd-PEt3

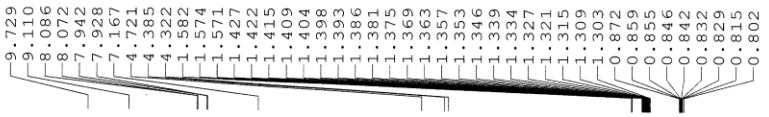
7

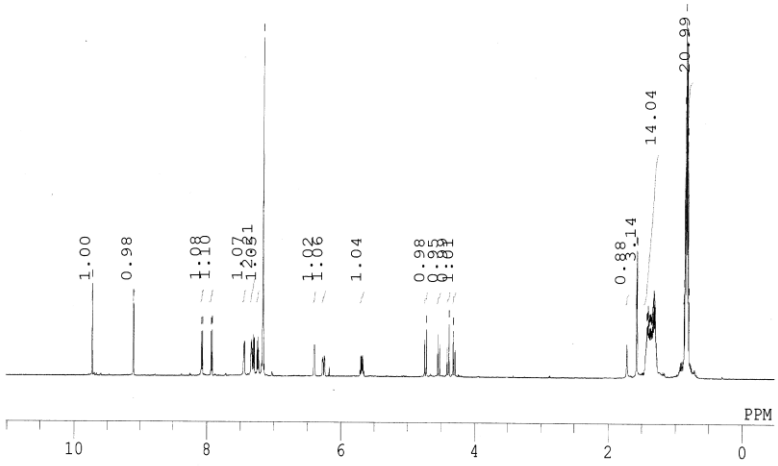

9.267
8.753
8.095
8.082
7.917
7.903
7.492
7.481
7.469
7.464
7.450
7.439
7.428
7.418
7.332
7.322
7.319
7.260
7.251
7.248
7.244
7.240
7.236
7.233
4.449
4.392
1.597
1.592
1.585
1.579
1.573
1.567
1.562
1.555
1.550
1.543
1.489
1.482
1.477
1.471
1.465
1.459
1.453
1.447
1.440
1.435
1.255
0.997
0.978
0.966
0.952
0.939
0.926
0.001
18.85
12.73
3.85
3.30
1.00
1.09
1.04
1.06
1.03
PPM
10
8
6
4
2
0

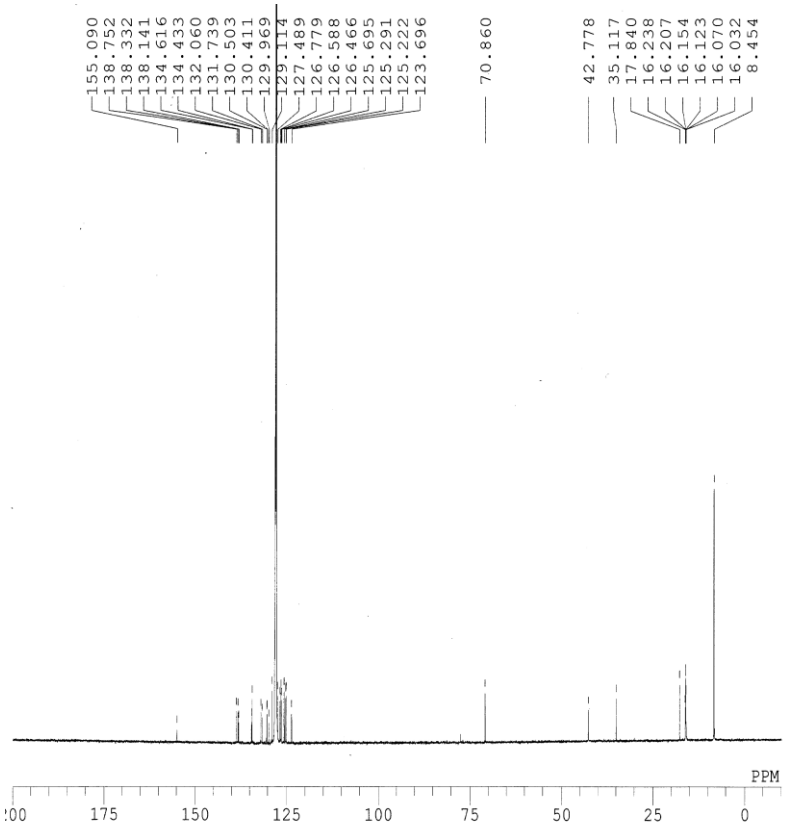

157.581
157.562
139.207
137.800
137.388
137.359
137.340
137.273
136.814
132.840
132.026
131.413
130.992
130.331
128.282
127.392
126.454
126.396
126.339
125.458
125.391
100.774
77.211
77.000
76.789
44.838
41.908
16.851
16.756
16.669
8.512
PPM
200
175
150
125
100
75
50
25
0

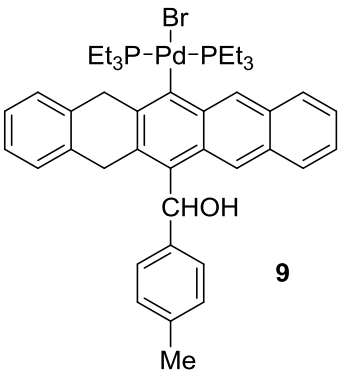

Br
Et3P-Pd-PEt3
CHOH

8

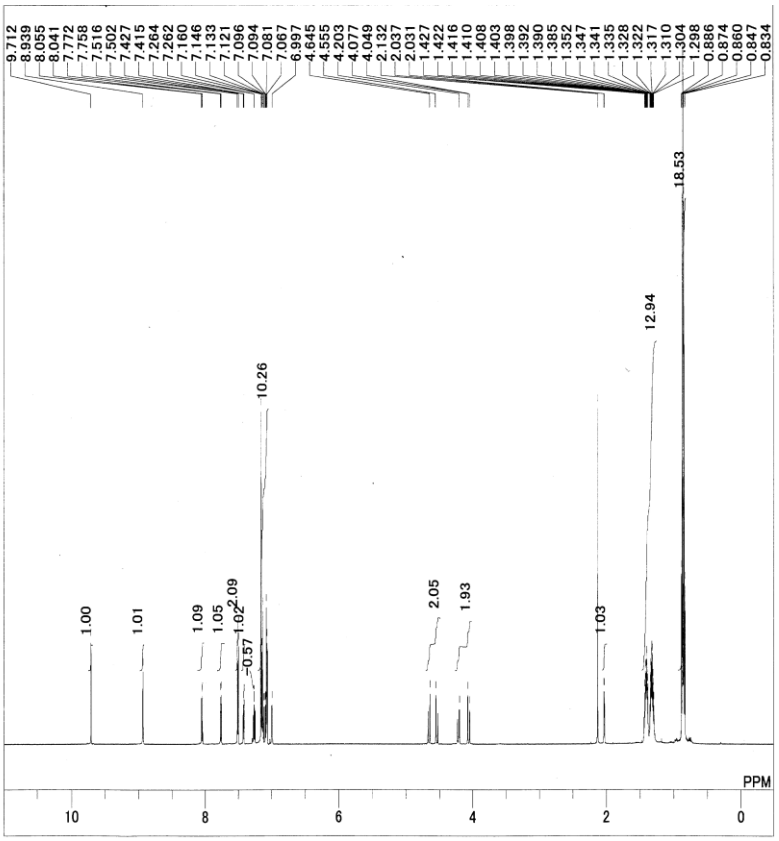

9.729
9.110
8.086
8.072
7.942
7.928
7.167
4.721
4.385
4.322
1.582
1.574
1.571
1.427
1.422
1.415
1.409
1.404
1.398
1.393
1.386
1.381
1.375
1.369
1.363
1.357
1.353
1.346
1.339
1.334
1.327
1.321
1.315
1.309
1.303
0.872
0.859
0.855
0.846
0.842
0.832
0.829
0.815
0.802

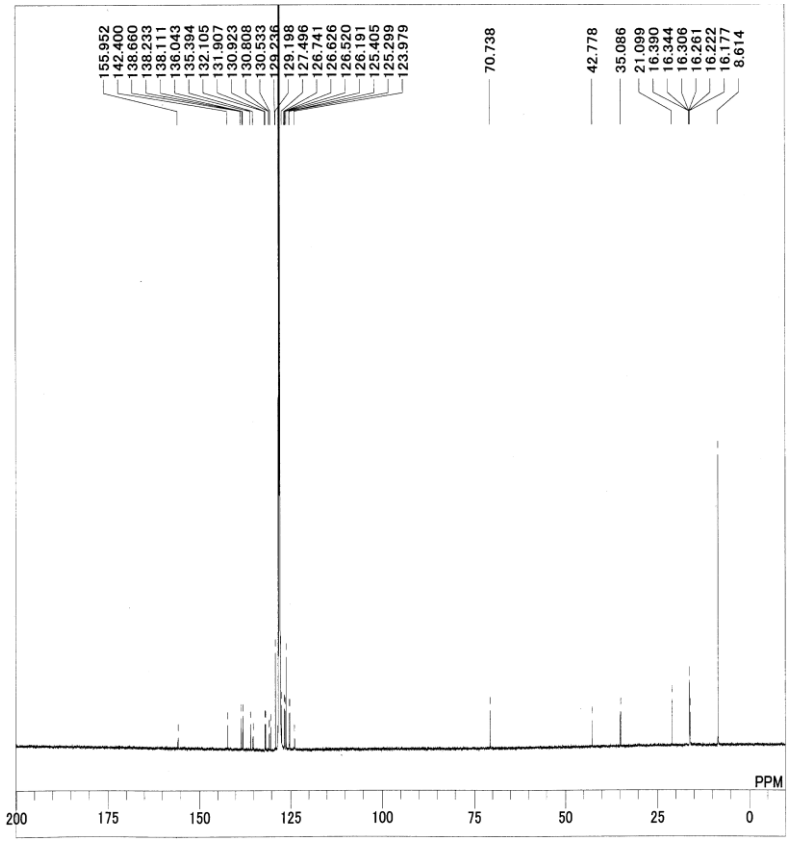

1.00
0.98
1.08
1.07
1.02
1.04
0.98
0.88
3.14
14.04
20.99
PPM
10
8
6
4
2
0

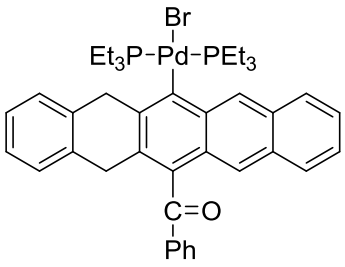

155.090
138.752
138.332
138.141
134.616
134.433
132.060
131.739
130.503
130.411
129.969
129.114
127.489
126.779
126.588
126.466
125.695
125.291
125.222
123.696
70.860
42.778
35.117
17.840
16.238
16.207
16.154
16.123
16.070
16.032
8.454
PPM
175
150
125
100
75
50
25
0


Br
Et3P-Pd-PEt3
CHOH
Me

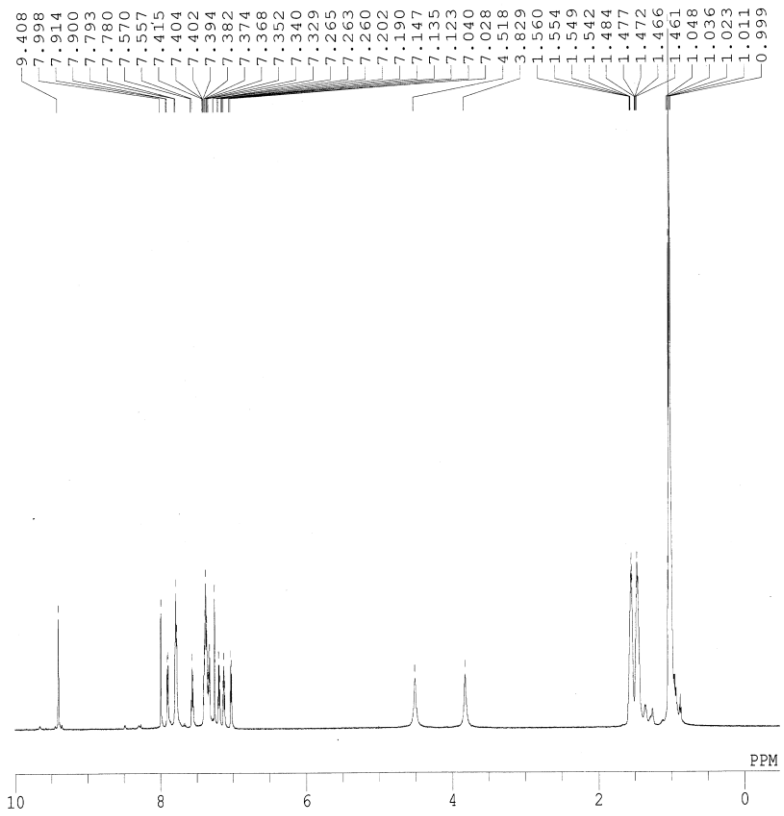
9

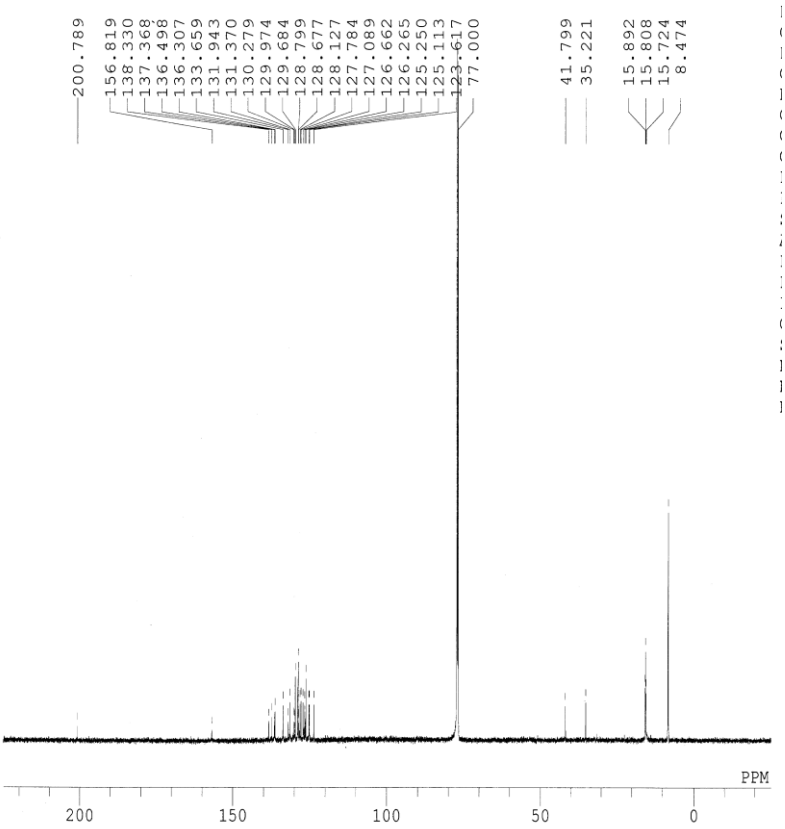

9.712
8.939
8.055
8.041
7.772
7.758
7.516
7.502
7.427
7.415
7.264
7.262
7.160
7.146
7.133
7.121
7.096
7.094
7.081
7.067
6.997
4.645
4.555
4.203
4.077
4.049
2.132
2.037
2.031
1.427
1.422
1.416
1.410
1.408
1.403
1.398
1.392
1.390
1.385
1.352
1.347
1.341
1.335
1.328
1.322
1.317
1.310
1.304
1.298
0.886
0.874
0.860
0.847
0.834
18.53
12.94
10.26
1.00
1.01
1.09
1.05
1.02
2.09
0.57
2.05
1.93
1.03
PPM
10
8
6
4
2
0

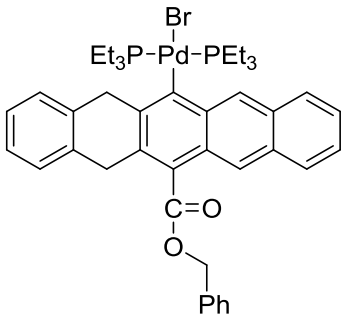

155.952
142.400
138.660
138.233
138.111
136.043
135.394
132.105
131.907
130.923
130.808
130.533
129.236
129.198
127.496
126.741
126.626
126.520
126.191
125.405
125.299
123.979
70.738
42.778
35.086
21.099
16.390
16.344
16.306
16.261
16.222
16.177
8.614
PPM
200
175
150
125
100
75
50
25
0


Br
Et3P-Pd-PEt3
C=O
Ph

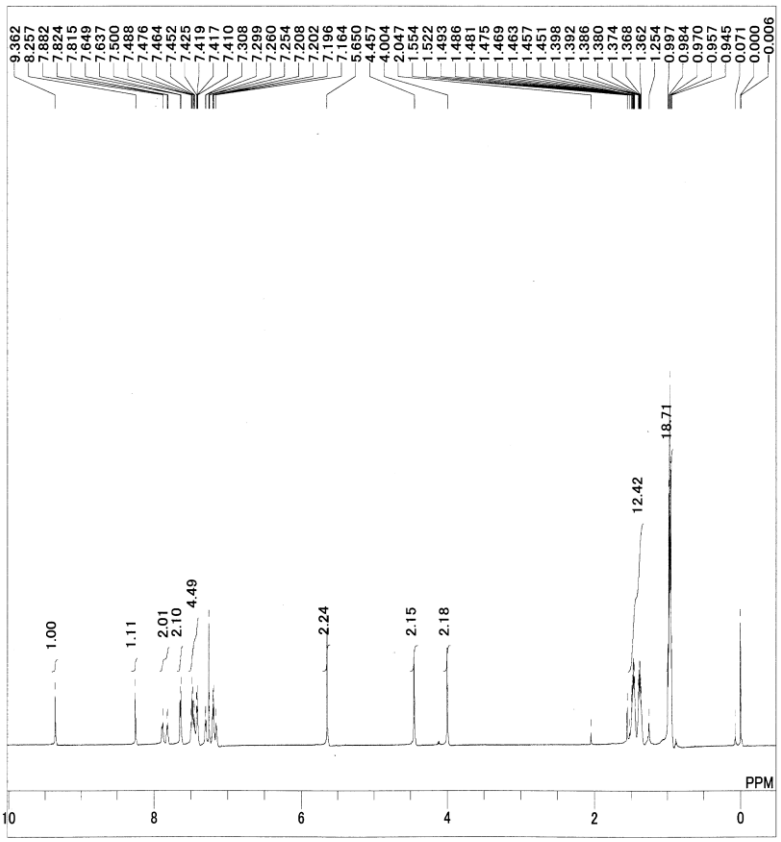
10

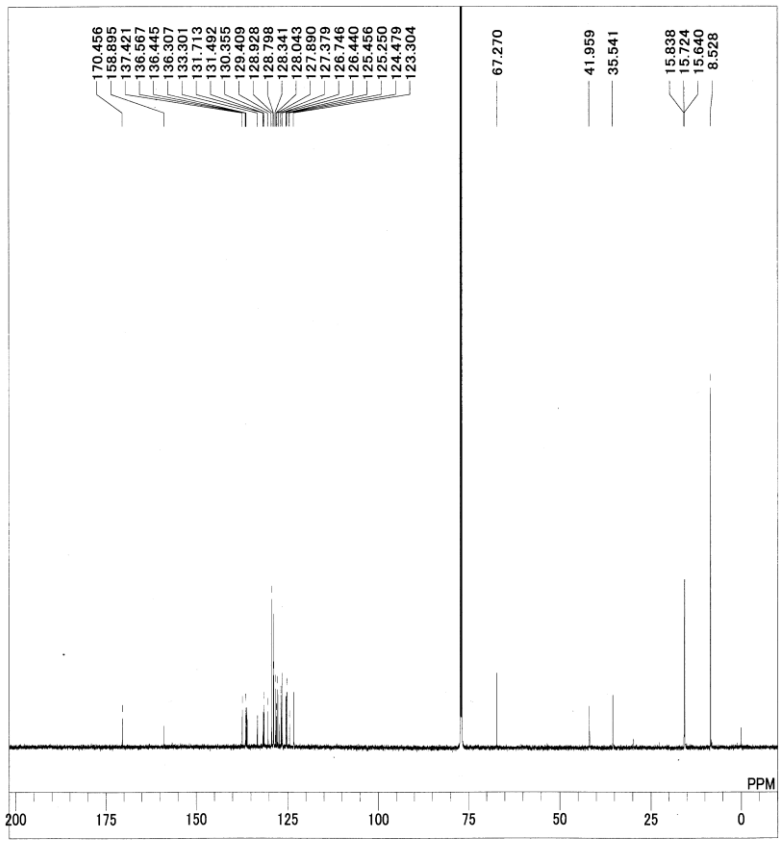

9.408
7.998
7.914
7.900
7.793
7.780
7.570
7.557
7.415
7.404
7.402
7.394
7.382
7.374
7.368
7.352
7.340
7.329
7.265
7.263
7.260
7.202
7.190
7.147
7.135
7.123
7.040
7.028
4.518
3.829
1.560
1.554
1.549
1.542
1.484
1.477
1.472
1.466
1.461
1.048
1.036
1.023
1.011
0.999
PPM
10
8
6
4
2
0

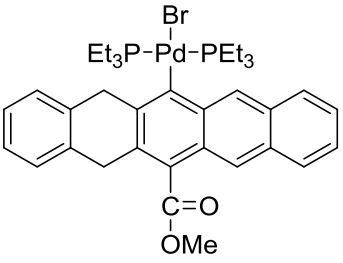

200.789
156.819
138.330
137.368
136.498
136.307
133.659
131.943
131.370
130.279
129.974
129.684
128.799
128.677
128.127
127.784
127.089
126.662
126.265
125.250
125.113
123.617
77.000
41.799
35.221
15.892
15.808
15.724
8.474
PPM
200
150
100
50
0


Br
Et3P-Pd-PEt3
C=O
O
Ph

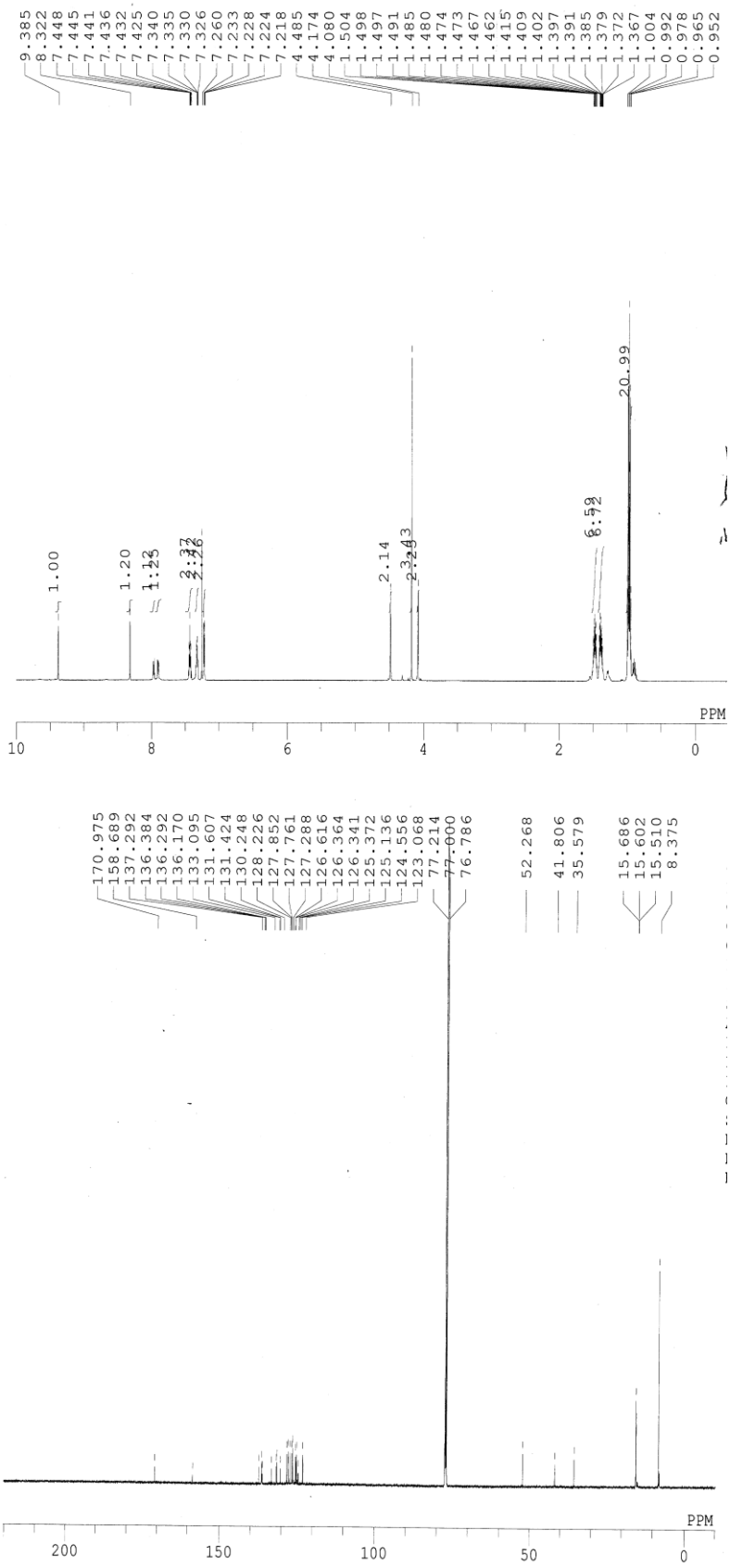
11

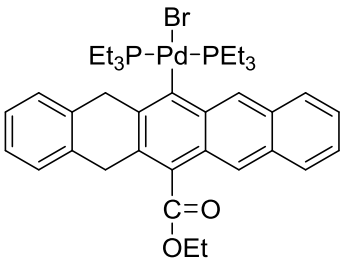

9.362
8.257
7.882
7.824
7.815
7.649
7.637
7.500
7.488
7.476
7.464
7.452
7.425
7.419
7.417
7.410
7.308
7.299
7.260
7.254
7.208
7.202
7.196
7.164
5.650
4.457
4.004
2.047
1.554
1.522
1.493
1.486
1.481
1.475
1.469
1.463
1.457
1.451
1.398
1.392
1.386
1.380
1.374
1.368
1.362
1.254
0.997
0.984
0.970
0.957
0.945
0.071
0.000
-0.006
1.00
1.11
2.01
2.10
4.49
2.24
2.15
2.18
12.42
18.71
PPM
10
8
6
4
2
0


170.456
158.895
137.421
136.567
136.445
136.307
133.301
131.713
131.492
130.355
129.409
128.928
128.798
128.341
128.043
127.890
127.379
126.746
126.440
125.456
125.250
124.479
123.304
67.270
41.959
35.541
15.838
15.724
15.640
8.528
PPM
200
175
150
125
100
75
50
25
0

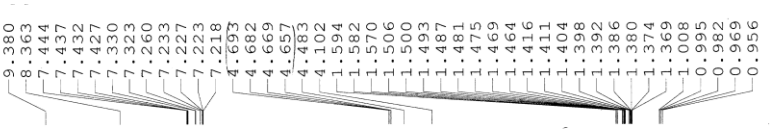

Br
Et3P-Pd-PEt3
C=O
OMe

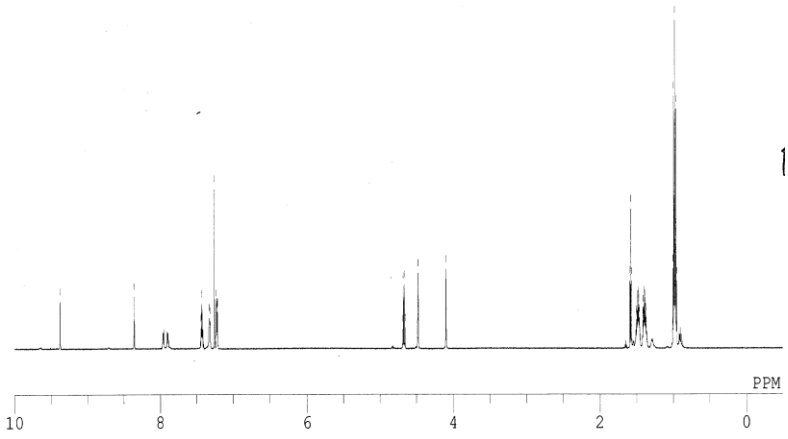
12

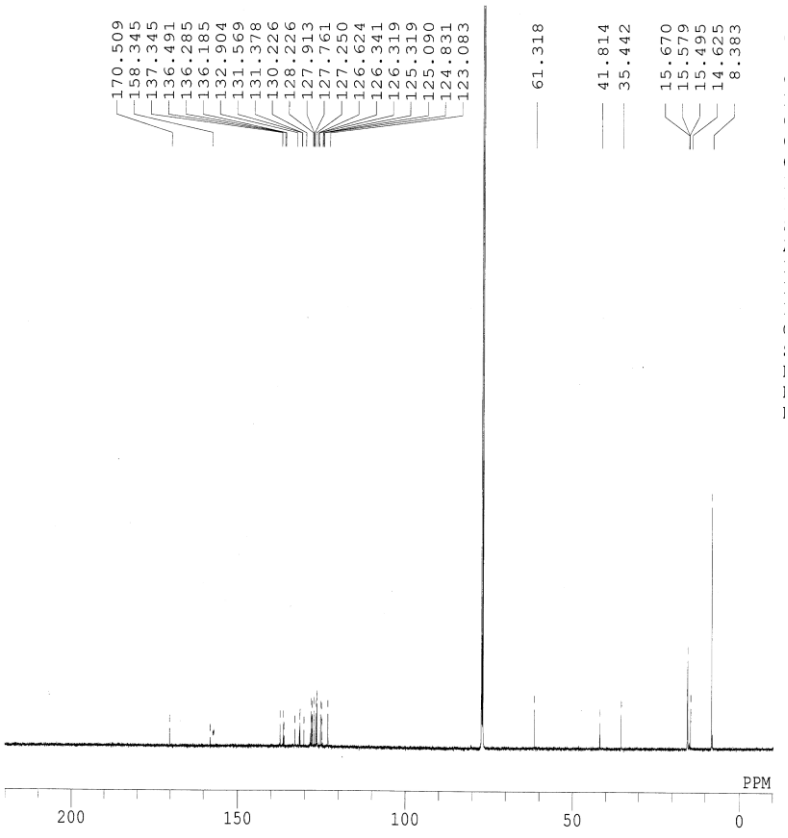

9.385
8.322
7.448
7.445
7.441
7.436
7.432
7.425
7.340
7.335
7.330
7.326
7.260
7.233
7.228
7.224
7.218
4.485
4.174
4.080
1.504
1.498
1.497
1.491
1.485
1.480
1.474
1.473
1.467
1.462
1.415
1.409
1.402
1.397
1.391
1.385
1.379
1.372
1.367
1.004
0.992
0.978
0.965
0.952
1.00
1.20
2.14
20.99
PPM
10
8
6
4
2
0
170.975
158.689
137.292
136.384
136.292
136.170
133.095
131.607
131.424
130.248
128.226
127.852
127.761
127.288
126.616
126.364
126.341
125.372
125.136
124.556
123.068
77.214
77.000
76.786
52.268
41.806
35.579
15.686
15.602
15.510
8.375
PPM
200
150
100
50
0

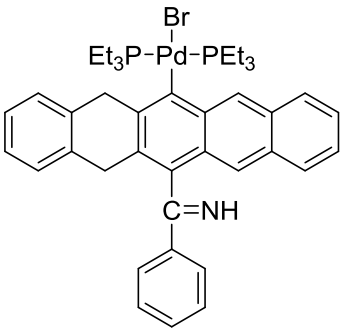

Br
Et3P-Pd-PEt3
C=O
OEt

13

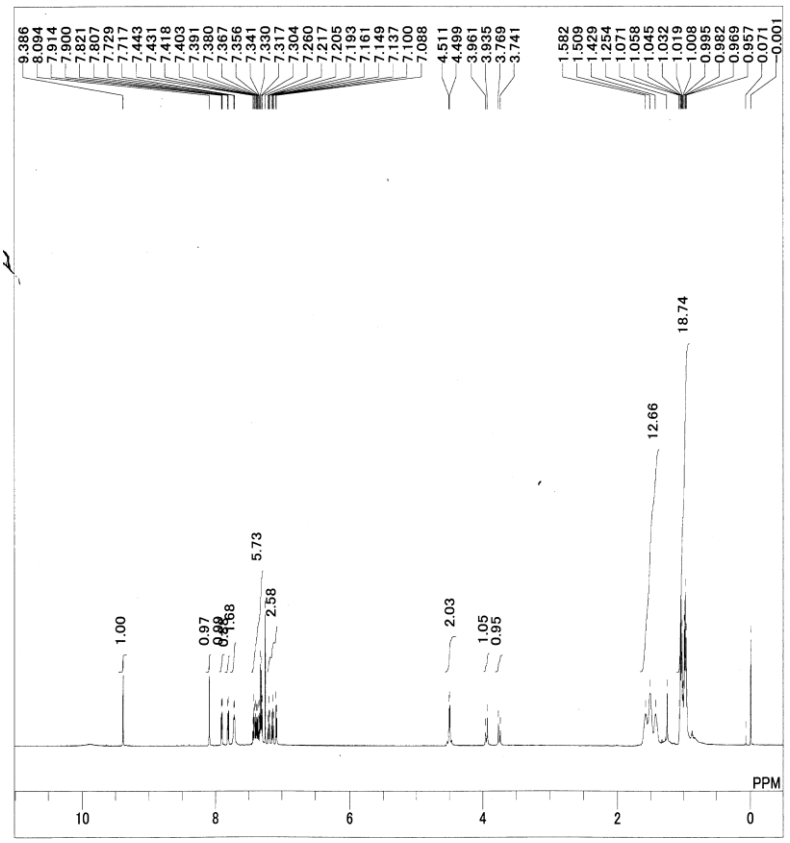

9.380
8.363
7.444
7.437
7.432
7.427
7.330
7.323
7.260
7.233
7.227
7.223
7.218
4.693
4.682
4.669
4.657
4.483
4.102
1.594
1.582
1.570
1.506
1.500
1.493
1.487
1.481
1.475
1.469
1.464
1.416
1.411
1.404
1.398
1.392
1.386
1.380
1.374
1.369
1.008
0.995
0.982
0.969
0.956

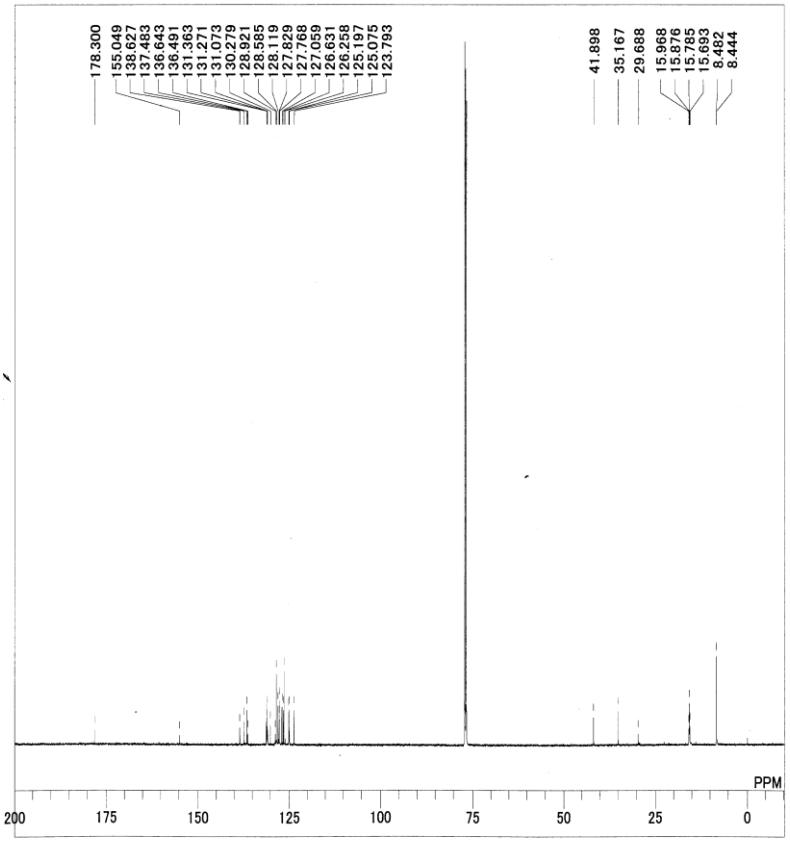

PPM
10
8
6
4
2
0

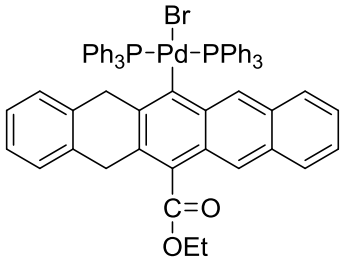

170.509
158.345
137.345
136.491
136.285
136.185
132.904
131.569
131.378
130.226
128.226
127.913
127.761
127.250
126.624
126.341
126.319
125.319
125.090
124.831
123.083
61.318
41.814
35.442
15.670
15.579
15.495
14.625
8.383
PPM
200
150
100
50
0


Br
Et3P-Pd-PEt3
C=NH

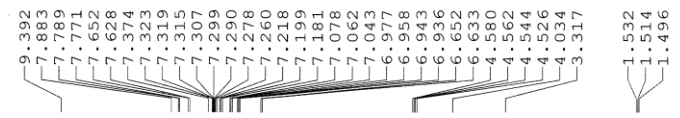
14

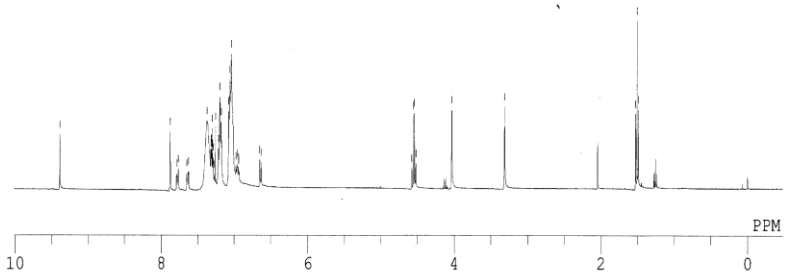

9.386
8.094
7.914
7.900
7.821
7.807
7.729
7.717
7.443
7.431
7.418
7.403
7.391
7.380
7.367
7.356
7.341
7.330
7.317
7.304
7.260
7.217
7.205
7.193
7.161
7.149
7.137
7.100
7.088
4.511
4.499
3.961
3.935
3.769
3.741
1.582
1.506
1.429
1.254
1.071
1.058
1.045
1.032
1.019
1.008
0.995
0.982
0.969
0.957
0.071
0.001
18.74
12.66
5.73
2.58
2.03
1.05
1.00
0.95
0.97
1.68
PPM
10
8
6
4
2
0

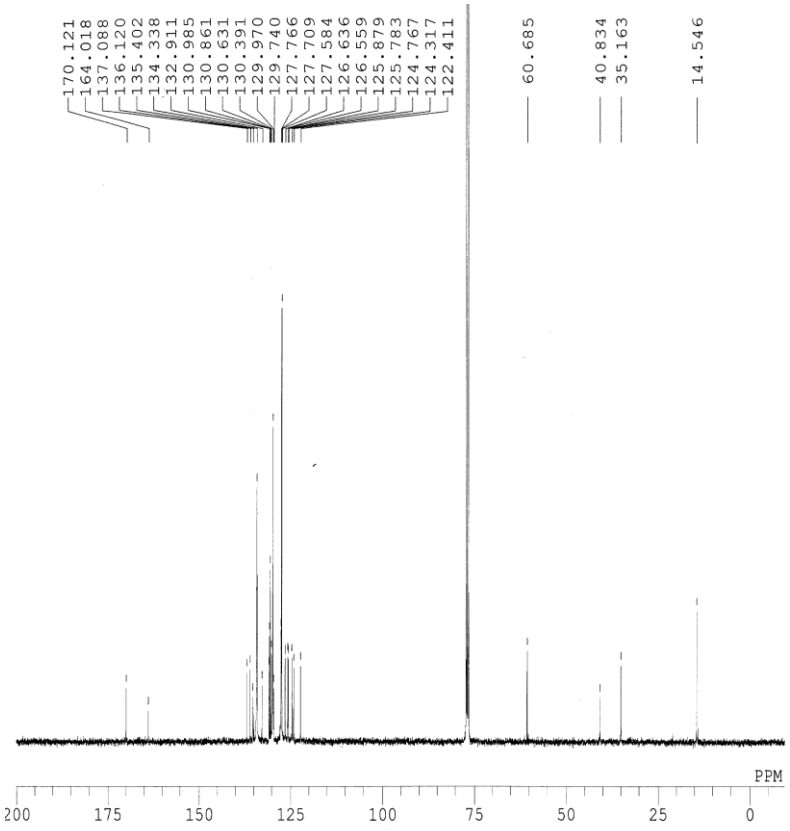

178.300
155.049
138.627
137.483
136.643
136.491
131.363
131.271
131.073
130.279
128.921
128.585
128.119
127.829
127.768
127.059
126.631
126.258
125.197
125.075
123.793
41.898
35.167
29.688
15.968
15.876
15.785
15.693
8.482
8.444
PPM
200
175
150
125
100
75
50
25
0

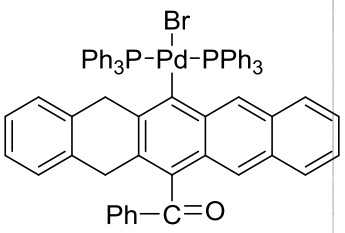

Br
Ph3P-Pd-PPh3
C=O
OEt

16

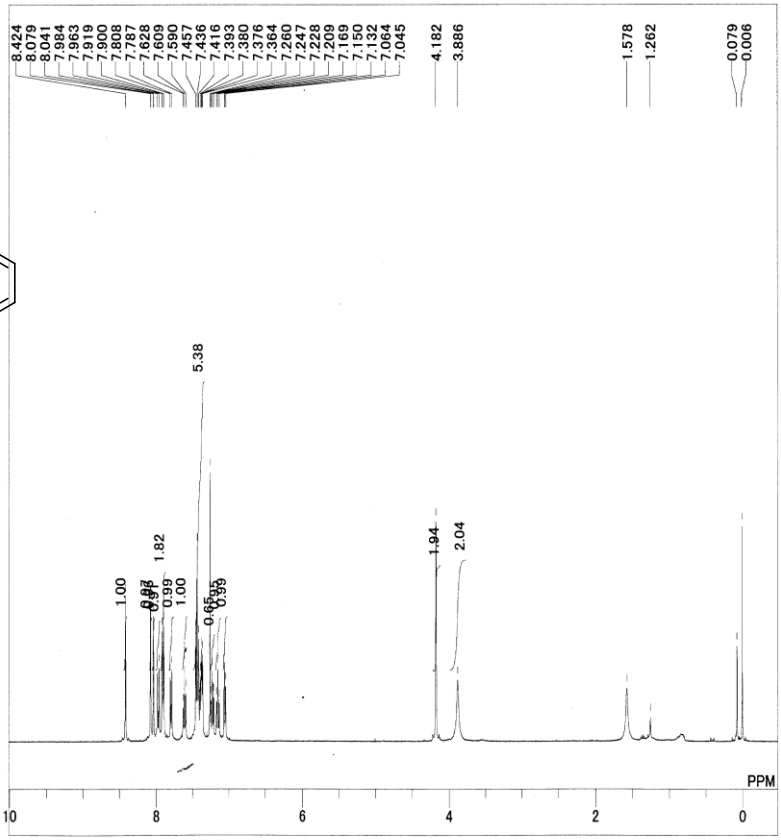

9.392
7.883
7.789
7.771
7.652
7.628
7.374
7.323
7.319
7.315
7.307
7.299
7.290
7.278
7.260
7.218
7.199
7.181
7.078
7.062
7.043
6.977
6.958
6.943
6.936
6.652
6.633
4.580
4.562
4.544
4.526
4.034
3.317
1.532
1.514
1.496

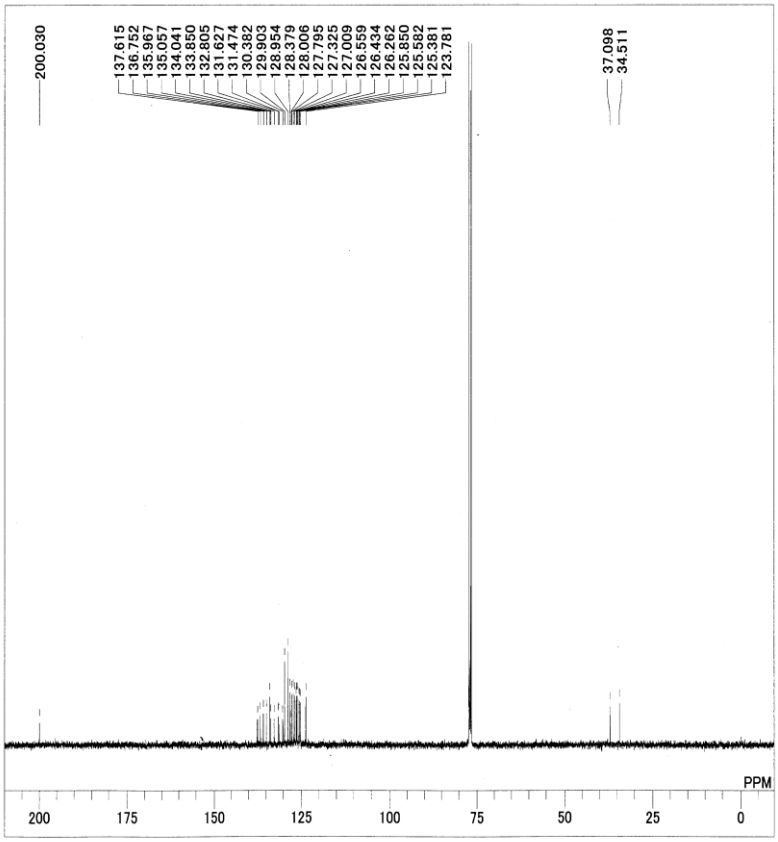

PPM
10
8
6
4
2
0

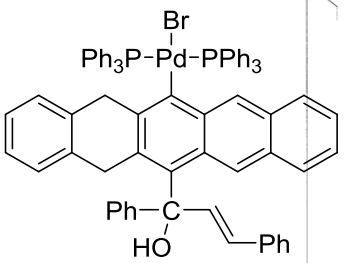

170.121
164.018
137.088
136.120
135.402
134.338
132.911
130.985
130.861
130.631
130.391
129.970
129.740
127.766
127.709
127.584
126.636
126.559
125.879
125.783
124.767
124.317
122.411
60.685
40.834
35.163
14.546
PPM
200
175
150
125
100
75
50
25
0


Br
Ph3P-Pd-PPh3
Ph—C=O

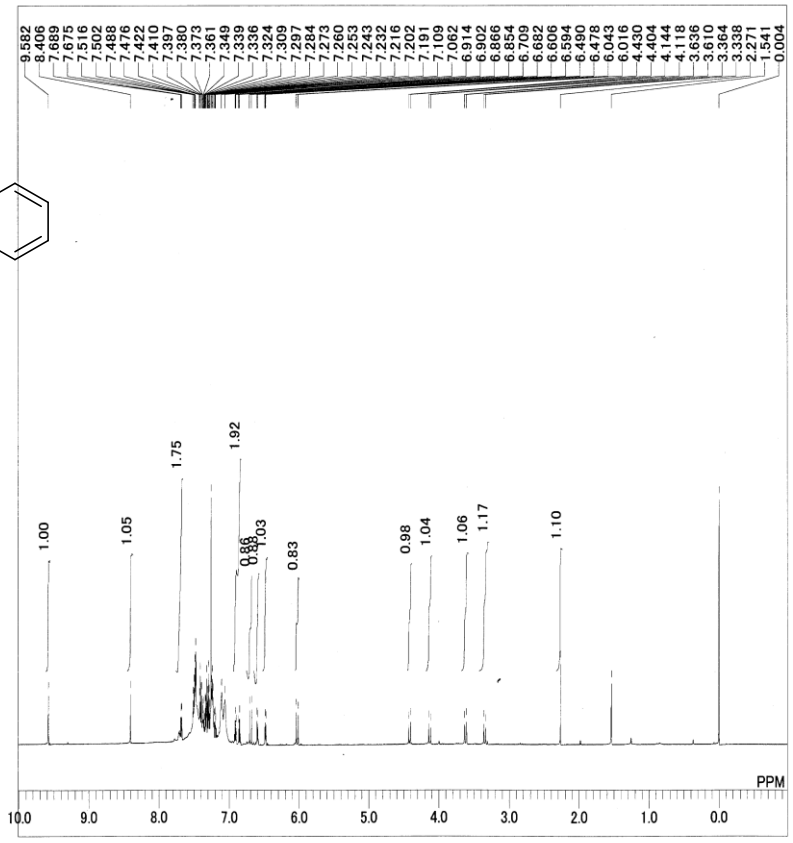
17

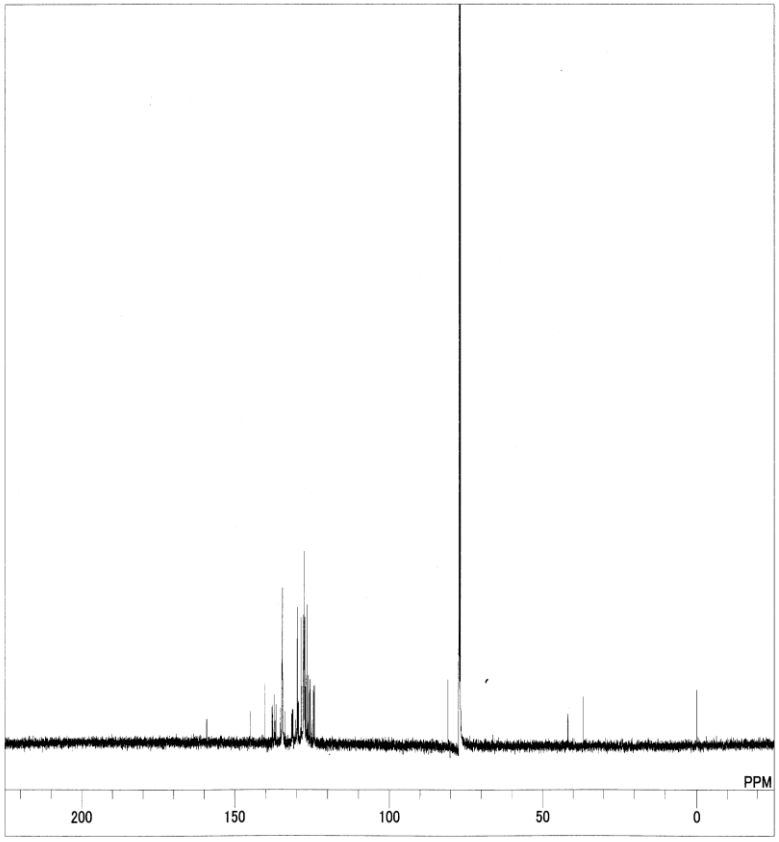

8.424
8.079
8.041
7.984
7.963
7.919
7.900
7.808
7.787
7.628
7.609
7.590
7.457
7.436
7.416
7.393
7.380
7.376
7.364
7.260
7.247
7.228
7.209
7.169
7.150
7.132
7.064
7.045
4.182
3.886
1.578
1.262
0.079
0.006
5.38
1.82
1.94
2.04
1.00
0.99
1.00
0.65
PPM
10
8
6
4
2
0

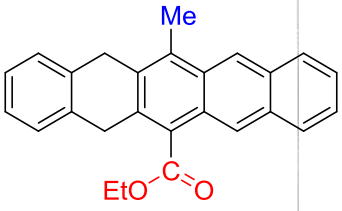

200.030
137.615
136.752
135.967
135.057
134.041
133.850
132.805
131.627
131.474
130.382
129.903
128.854
128.379
128.006
127.795
127.325
127.009
126.559
126.434
126.262
125.850
125.582
125.381
123.781
37.098
34.511
PPM
200
175
150
125
100
75
50
25
0


Br
Ph3P-Pd-PPh3
Ph—C
HO
Ph

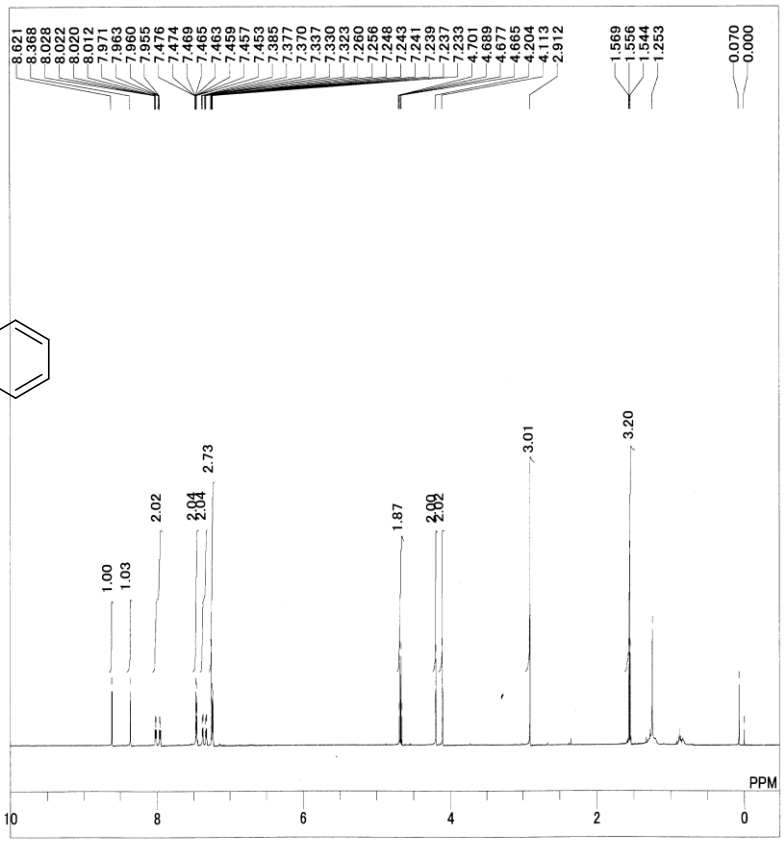
18

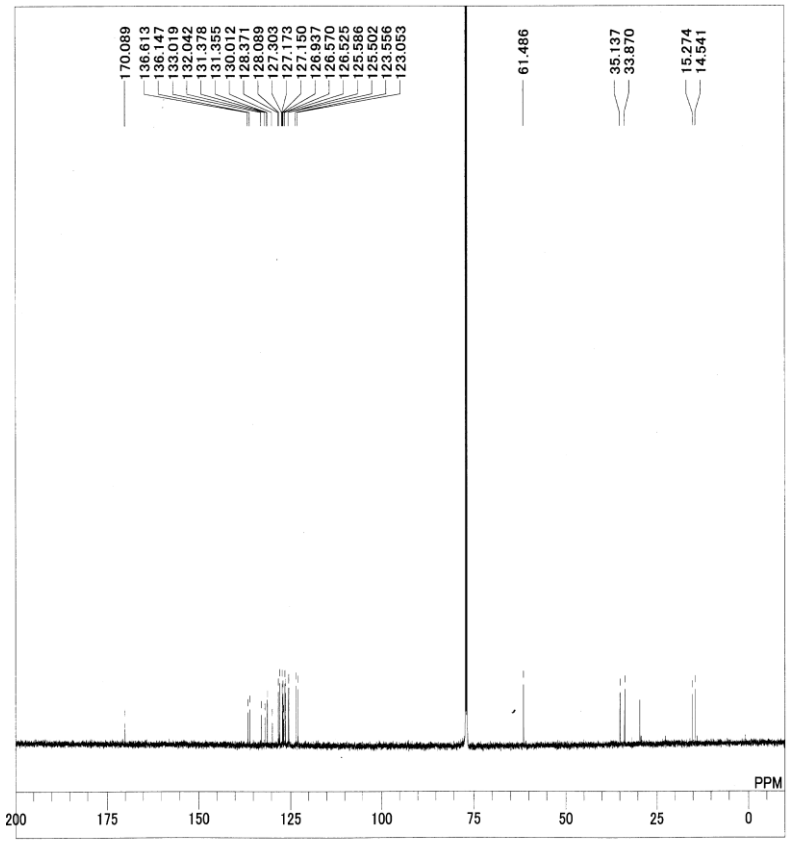

9.582
8.406
7.689
7.675
7.516
7.502
7.488
7.476
7.422
7.410
7.397
7.380
7.373
7.361
7.349
7.339
7.336
7.324
7.309
7.297
7.284
7.273
7.260
7.253
7.243
7.232
7.216
7.202
7.191
7.109
7.062
6.914
6.902
6.866
6.854
6.709
6.682
6.606
6.594
6.490
6.478
6.043
6.016
4.430
4.404
4.144
4.118
3.636
3.610
3.364
3.338
2.271
1.541
0.004
1.00
1.05
1.75
1.92
0.86
0.88
1.03
0.83
0.98
1.04
1.06
1.17
1.10
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

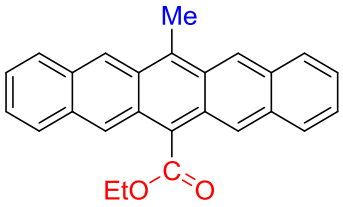

PPM
200
150
100
50
0


Me
EtO
C
O

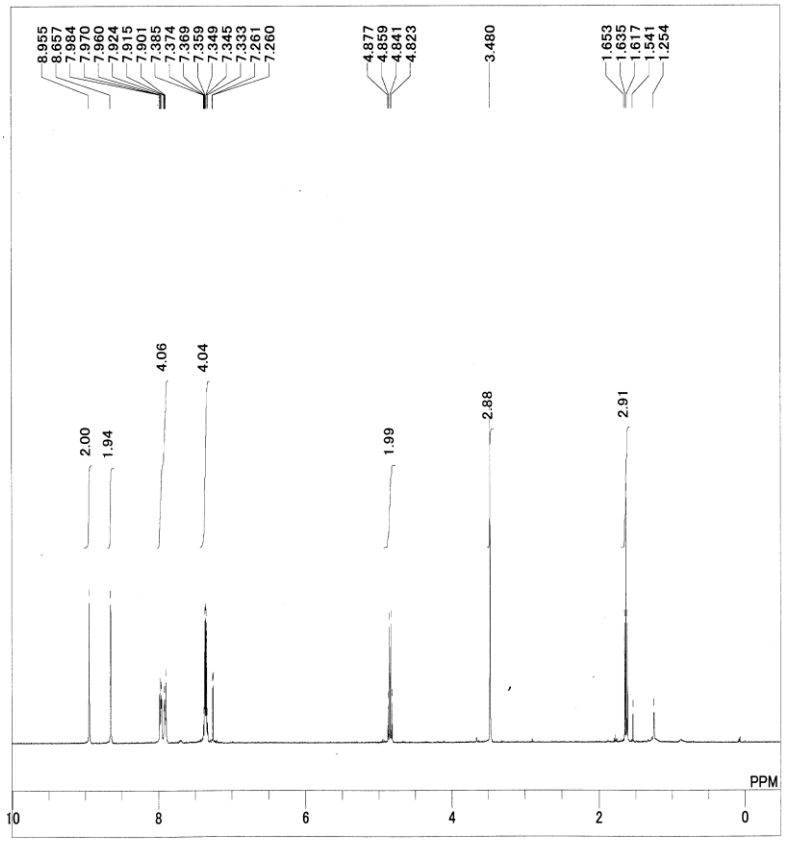
19

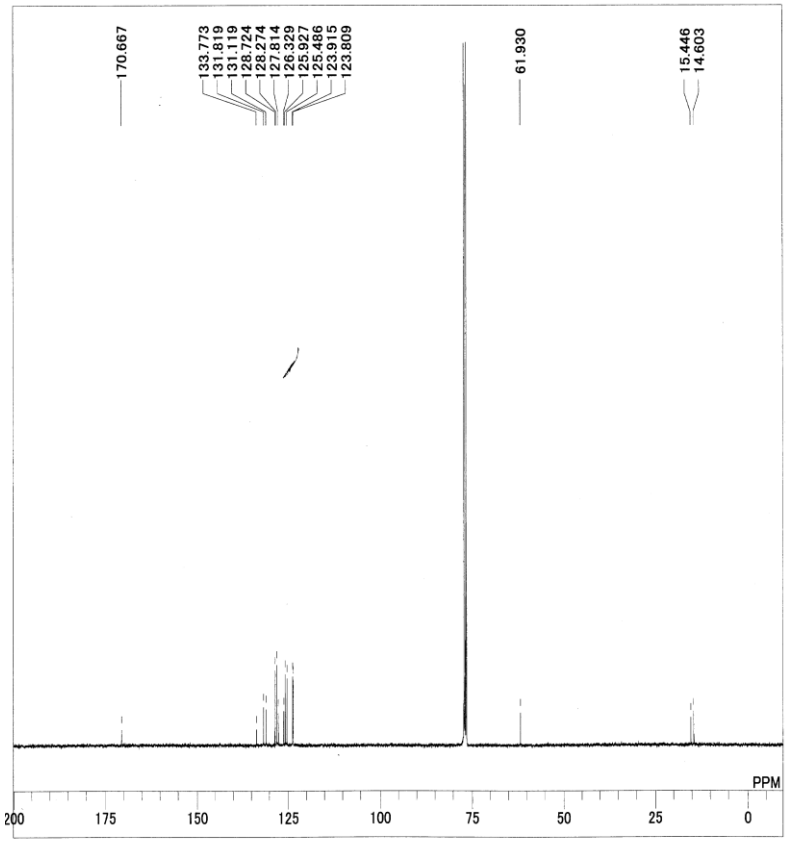

8.621
8.368
8.028
8.022
8.020
8.012
7.971
7.963
7.960
7.955
7.476
7.474
7.469
7.465
7.463
7.459
7.457
7.453
7.385
7.377
7.370
7.337
7.330
7.323
7.260
7.256
7.248
7.243
7.241
7.239
7.237
7.233
4.701
4.689
4.677
4.665
4.204
4.113
2.912
1.569
1.556
1.544
1.253
0.070
0.000
1.00
1.03
2.02
2.04
2.04
2.73
1.87
2.09
2.02
3.01
3.20
PPM
10
8
6
4
2
0

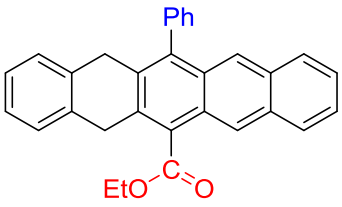

170.089
136.613
136.147
133.019
132.042
131.378
131.355
130.012
128.371
128.089
127.303
127.173
127.150
126.937
126.570
126.525
125.586
125.502
123.556
123.053
61.486
35.137
33.870
15.274
14.541
PPM
200
175
150
125
100
75
50
25
0


Me
EtO
C
O

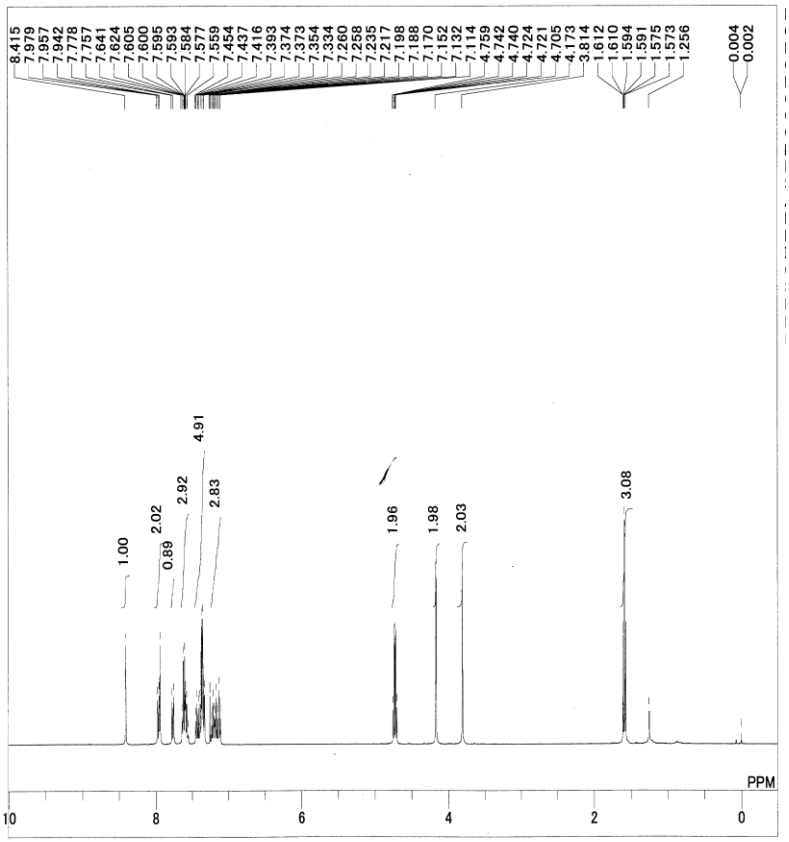
20

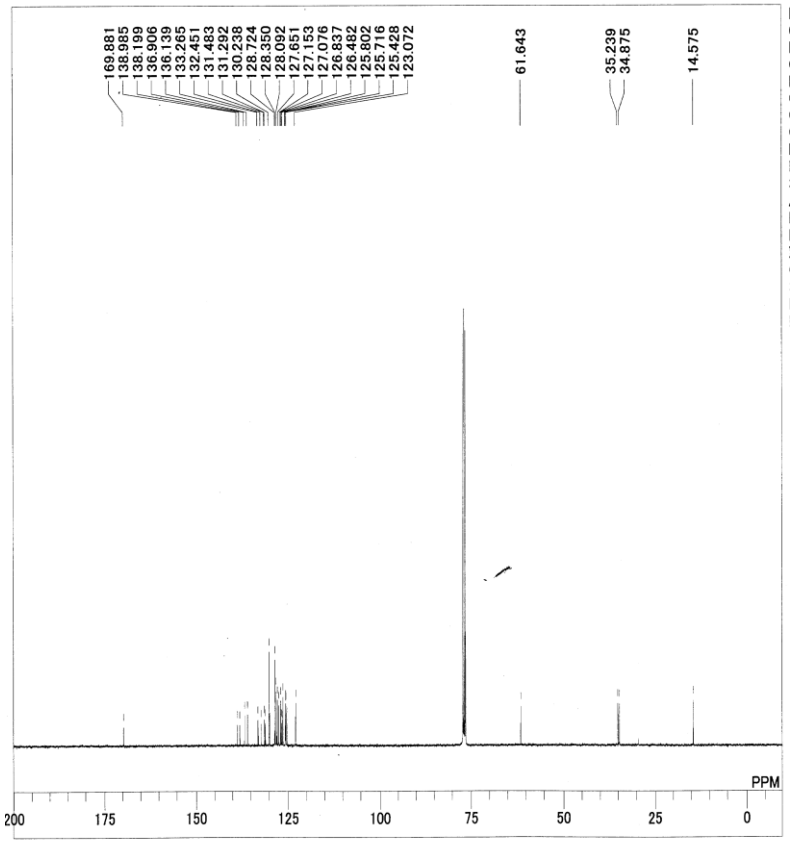

8.955
8.657
7.984
7.970
7.960
7.924
7.915
7.901
7.385
7.374
7.369
7.359
7.349
7.345
7.333
7.261
7.260
4.877
4.859
4.841
4.823
3.480
1.653
1.635
1.617
1.541
1.254
2.00
1.94
4.06
4.04
1.99
2.88
2.91
PPM
10
8
6
4
2
0

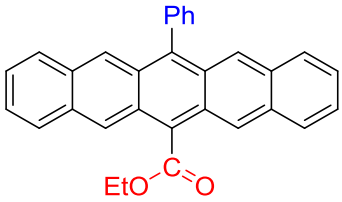

170.667
133.773
131.819
131.119
128.724
128.274
127.814
126.329
125.927
125.486
123.915
123.809
61.930
15.446
14.603
PPM
200
175
150
125
100
75
50
25
0


Ph
EtO
C
O

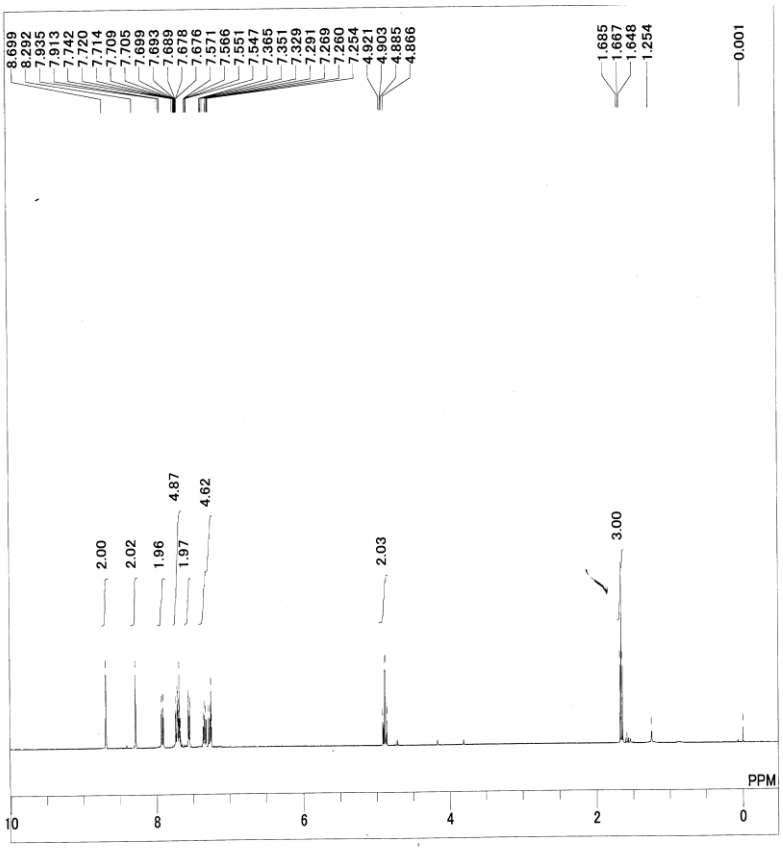
21

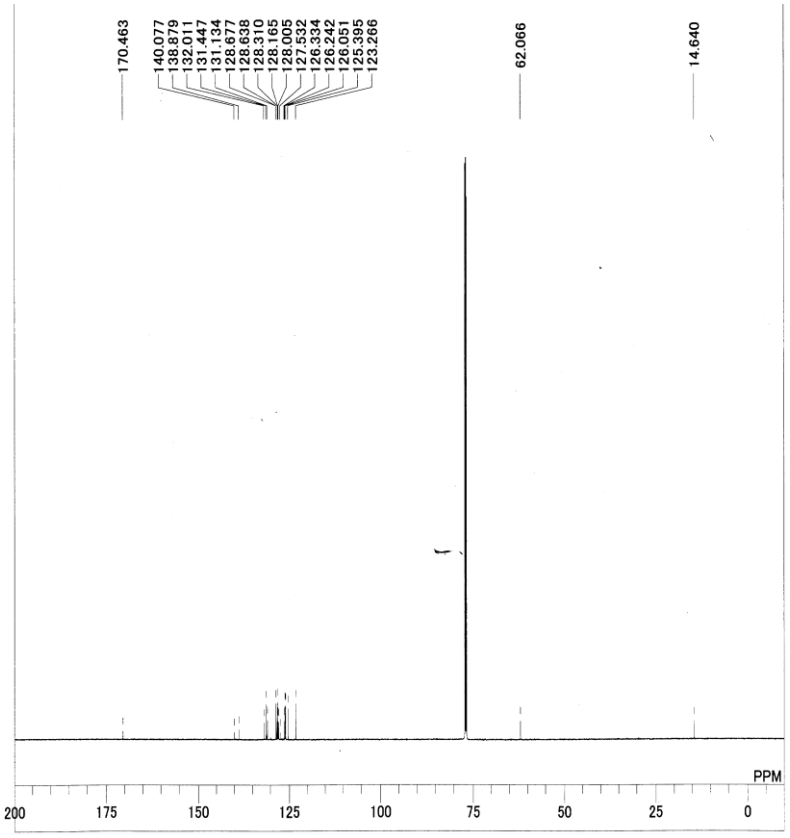

8.415
7.979
7.957
7.942
7.778
7.757
7.641
7.624
7.605
7.600
7.595
7.593
7.584
7.577
7.559
7.454
7.437
7.416
7.393
7.374
7.373
7.354
7.334
7.260
7.258
7.235
7.217
7.198
7.188
7.170
7.152
7.132
7.114
4.759
4.742
4.740
4.724
4.721
4.705
4.173
3.814
1.612
1.610
1.594
1.591
1.575
1.573
1.256
0.004
0.002
1.00
2.02
0.89
2.92
4.91
2.83
1.96
1.98
2.03
3.08
PPM
10
8
6
4
2
0

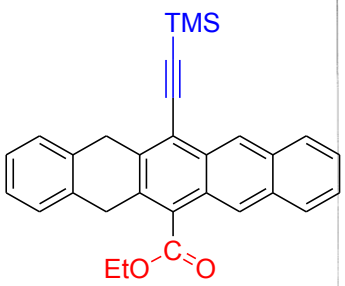

169.881
138.985
138.199
136.906
136.139
133.265
132.451
131.483
131.292
130.238
128.724
128.350
128.092
127.651
127.153
127.076
126.837
126.482
125.802
125.716
125.428
123.072
61.643
35.239
34.875
14.575
PPM
200
175
150
125
100
75
50
25
0


Ph
EtO
C
O

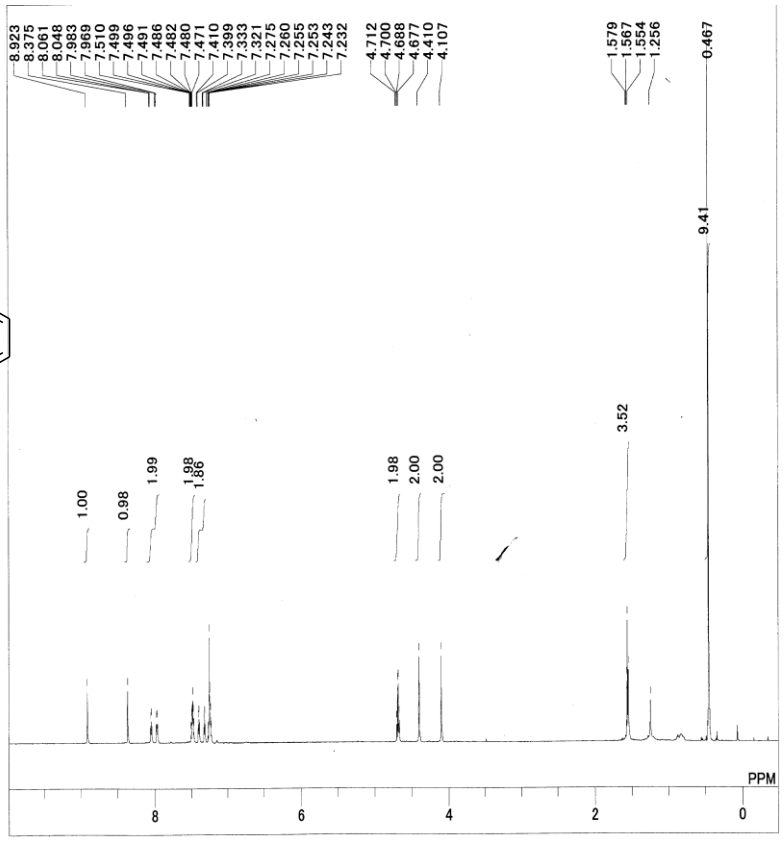
22

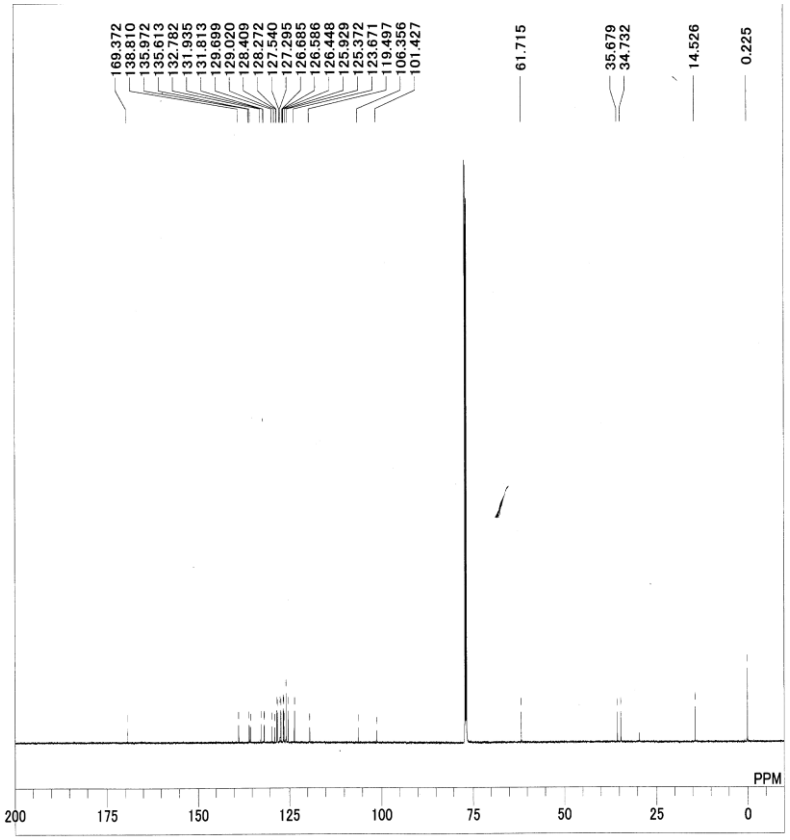

8.699
8.292
7.935
7.913
7.742
7.720
7.714
7.709
7.705
7.699
7.693
7.689
7.678
7.676
7.571
7.566
7.551
7.547
7.365
7.351
7.329
7.291
7.269
7.260
7.254
4.921
4.903
4.885
4.866
1.685
1.667
1.648
1.254
0.001
2.00
2.02
1.96
1.97
4.87
4.62
2.03
3.00
PPM
10
8
6
4
2
0

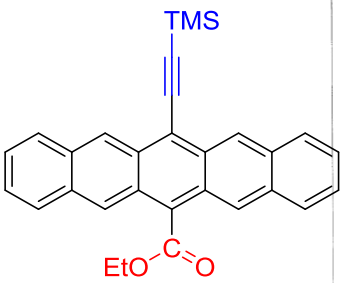

170.463
140.077
138.879
132.011
131.447
131.134
128.877
128.638
128.310
128.165
128.005
127.532
126.334
126.242
126.051
125.395
123.266
62.066
14.640
PPM
200
175
150
125
100
75
50
25
0


TMS
EtO
C
O

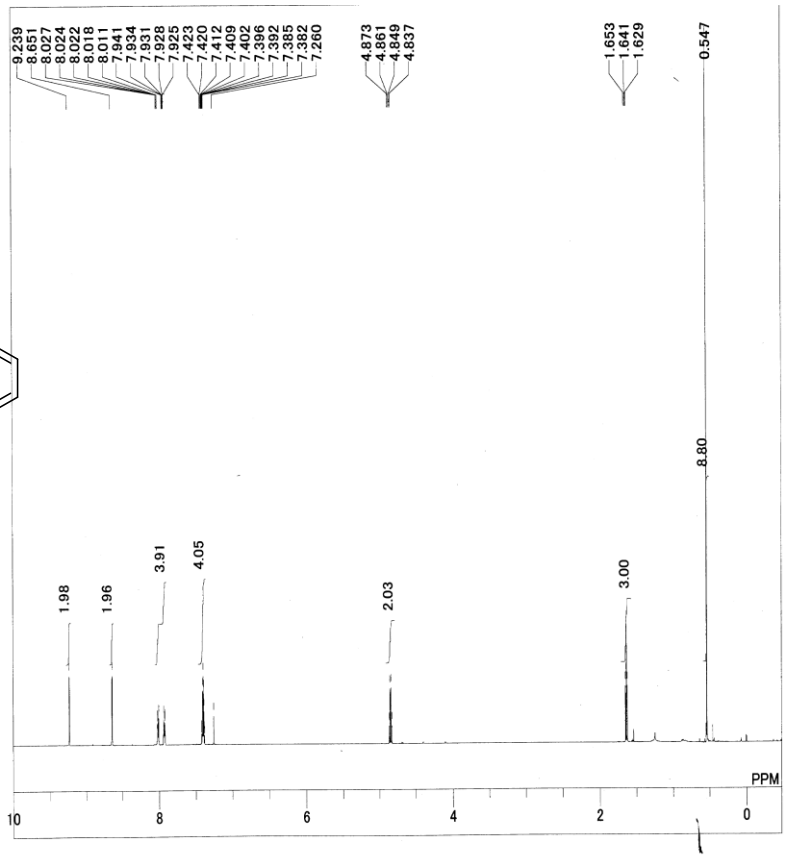
23

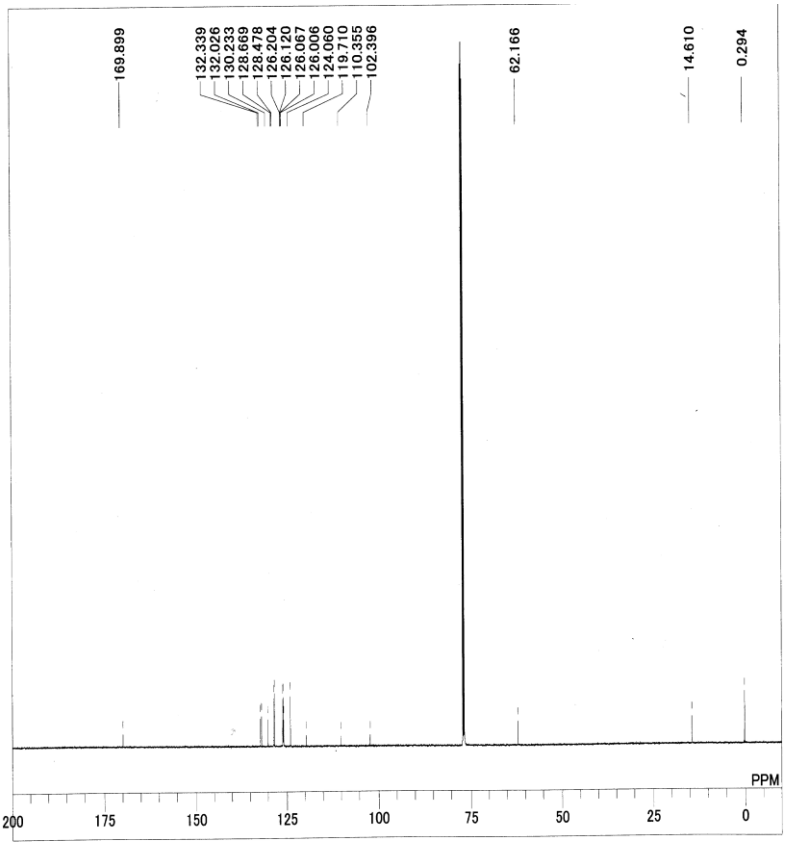

8.923
8.375
8.061
8.048
7.983
7.969
7.510
7.499
7.496
7.491
7.486
7.482
7.480
7.471
7.410
7.399
7.333
7.321
7.275
7.260
7.255
7.253
7.243
7.232
4.712
4.700
4.688
4.677
4.410
4.107
1.579
1.567
1.554
1.256
0.467
9.41
3.52
1.00
0.98
1.99
1.98
1.86
1.98
2.00
2.00
PPM
8
6
4
2
0


169.372
138.810
135.972
135.813
132.782
131.935
131.813
129.699
129.020
128.409
128.272
127.540
127.295
126.685
126.586
126.448
125.929
125.372
123.671
119.497
106.356
101.427
61.715
35.679
34.732
14.526
0.225
PPM
200
175
150
125
100
75
50
25
0


TMS
EtO
C
O

24


9.239
8.651
8.027
8.024
8.022
8.018
8.011
7.941
7.934
7.931
7.928
7.925
7.423
7.420
7.412
7.409
7.402
7.396
7.392
7.385
7.382
7.260
4.873
4.861
4.849
4.837
1.653
1.641
1.629
0.547
8.80
1.98
1.96
3.91
4.05
2.03
3.00
PPM
10
8
6
4
2
0


169.899
132.339
132.026
130.233
128.669
128.478
126.204
126.120
126.067
126.006
124.060
119.710
110.355
102.396
62.166
14.610
0.294
PPM
200
175
150
125
100
75
50
25
0